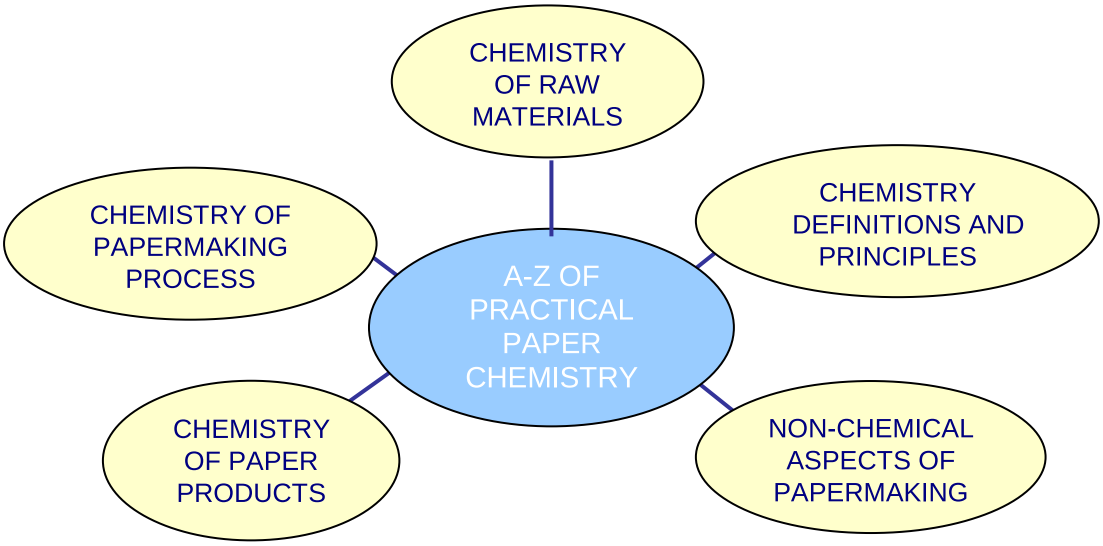
A-Z OF PRACTICAL PAPER CHEMISTRY



COMPILED BY LESLIE WEBB

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A-Z OF PRACTICAL PAPER CHEMISTRY, Envirocell, UK, 2003.

Webb, LJ "A-Z OF PRACTICAL PAPER CHEMISTRY", Version 1.0, 2003.

Introduction

It is somewhat puzzling (and embarrassing) to recall that, on graduating some years ago and keen to apply my hard-won chemical expertise, I had an interview with a since-closed paper mill. They didn’t get as far as offering me a job as I had no hesitation in informing them that I had no intention of working there as I failed to see where there was any chemistry in the process. Well, many years later, I can confirm that I was about as wrong as you can be, but, of course, the chemistry that does take place in papermaking is not the stuff that grabs the imagination of a young graduate - frothing test-tubes, big bangs or colourful crystals - exactly what you don't want at a paper mill in fact. With the benefit of hindsight, a job as a paper mill chemist would have involved much more real chemistry than the first job I did for about a year, particularly if you don't mind mixing your chemistry with some physics, engineering and microbiology.

Of course, the chemistry of papermaking is more to do with subtle interactions between what appear to be rather unexciting white or brown particles (fibres) and invisible (water-soluble) polymers all carried out in the presence of lots of water and its load of dissolved solids to add a little complexity to the interactions. It is normally axiomatic at the start of this sort of document to mention the complexity of the chemistry that does take place within a paper mill and this is undoubtedly true. Having devoted a considerable time to developing this document, I might have hoped to report a slight lessening of this complexity in my own mind, but I am sure that, as every scientist knows, this never seems to happen as you reveal yet more depths to investigate. And of course, this is what keeps you going.

So, paper chemistry is a vast subject and no single text can hope to do full justice to it and retain a reasonable length. Today, there are several excellent books devoted to the subject and probably hundreds of articles published every year to add to the literature of paper chemistry. This CD-rom brings together some of this information in a format that isn’t new in itself, but is new to paper chemistry. This is Version 1 and I am sure that everyone that browses through it will find (or rather not find) something that they think should be there, but isn’t. Hence, there will be future versions that take forward the concept and fill in some of those inevitable gaps and weaker areas.

Content

As summarised in the title and the graphic on the opening page, this document is about the chemistry of papermaking raw materials, of the papermaking process and of paper products. The chemistry of the manufacturing processes for every papermaking material is not covered in detail as the document would then be at least double the present length. It should be particularly noted that the chemistry of the various pulping processes is deliberately not covered in the same depth as the chemistry of papermaking itself, but they are covered in what is hopefully enough detail to understand the chemical character of the resulting pulps.

This document is intended for a wide audience from experienced papermakers with little formal training in chemistry to experienced chemists with little formal training in papermaking. To help people at either end of this spectrum, this document provides some basic definitions of non-chemical papermaking terms (for the chemists) and of some basic chemical terms (for the papermakers).

Viewing

The "look" of this document has been optimised for viewing in "page layout" or “print layout” view and it is recommended that the document is not viewed in "online layout" or “web layout” view as this changes the position of drawings/figures so that that they are no longer in the best place. The zoom level should be set so that the full width of the document is visible without the need to scroll across horizontally or just use the "fit to width" setting. The full-screen version gives the most information on the screen at any one time in any view format.

The text includes many graphs illustrating chemistry effects within papermaking. These graphs are either based on model projections or on data taken from published papers. Whilst care has been taken to reproduce the graphs as accurately as possible, they are included mainly to indicate overall trends. The reader should refer to the original paper where precise values need to be interpolated.

Navigation

A full list of the entries is included at the back of this document, but this is just for completeness as the best way to move around this document is not by looking down this list (they are not hyper-linked).

The best way to find a particular entry is by loading the document map from the View dropdown list, which will then appear as a side-bar down the left-hand side of the screen in any viewing format. You can scroll down the document map and click on any item listed in it. The width of the document map can be altered by dragging its right-hand margin when it appears in the cross-hairs. Once in a particular entry, there are hyper-linked words and phrases to take you to a related topic, but note that A-Z entry words that appear in the text are not always hyper-linked. With the Web toolbar loaded from the View dropdown list, you can also use the normal back and forward buttons.

If you cannot find the subject in the document map, there may be still be information on it within the text and the easiest way to find out is to use "Find" in the Edit dropdown list (or Control + F) and type in the relevant word or words - there is no need for a sophisticated search engine in a single document of this size.

Here are some useful starting points for the general browser:

Chemistry is a useful starting point for the non-chemist if you want to learn some of the basics of this enormous subject.

Papermaking is a useful starting point if you want to learn the basics of the processes involved without too much emphasis on chemistry.

Paper products is a useful starting point if you want to learn about the chemistry of the final products.

The Periodic Table is a useful starting point if you want to see what elements feature in papermaking raw materials and products.

Raw materials is a useful starting point if you wish to explore the general sorts of substances that go into paper products from the view[point of their functionality.

Acknowledgements

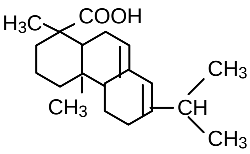
The writer is grateful to everyone who has contributed to this document unknowingly by publishing the results of their researches and investigations.

Disclaimer

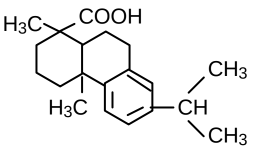
The author accepts no liability whatsoever for any use to which the information in this document is put. The onus is on the reader to use their own judgement and knowledge to check the applicability of the information provided to their own situation.

Abietic acids

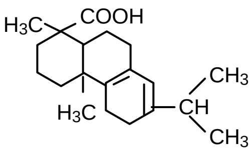
This is one of the two groups of mono-carboxylic acids that comprise the resin acids, which is part of the extractives fraction of wood. After pulping/bleaching, some resin acids may remain with the papermaking pulp as part of its pitch fraction. Abietic acids are also one of the main components of rosin size. There are a number of acids in this general group, which are distinguished from the pimaric acids by having an iso-propyl group (rather than methyl and vinyl groups) in the third ring. The main abietic acids are shown below:



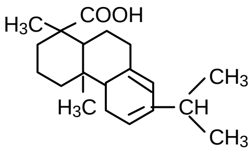
Abietic acid



Dehydroabietic acid



Palustrinic acid



Levo-pimaric acid

It is evident that the main difference between each acid is the number and position of the double bonds. Somewhat confusingly, one of the abietic acids is levo-pimaric acid, the 1,4-diene structure of which allows a Diels-Alder reaction to be carried out to fortify rosin products for sizing. The acids can quite easily isomerise between one another and the double bonds can be oxidised - for example by atmospheric oxygen, which causes the acid to darken in colour. Ionisation of the acids in papermaking causes problems both for pitch and rosin sizing, the pK_A value of abietic acid being about 5.2 at 25^{o}C.

Absorbency

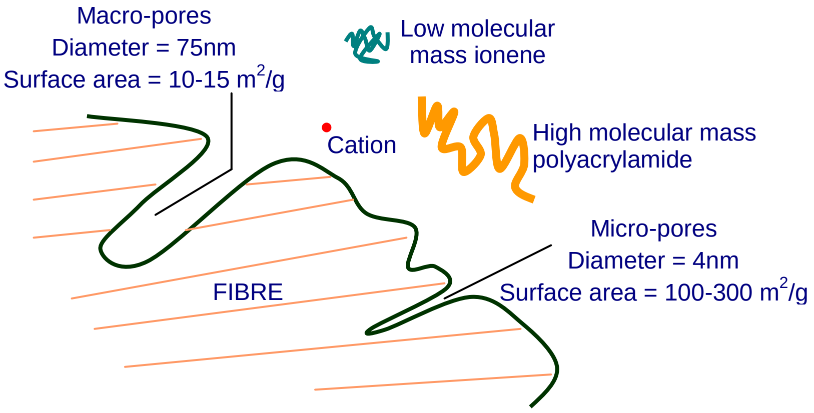
This is the ability to absorb liquids and is an important attribute for certain paper grades such as tissues, towels, blotting paper, etc. Papers that are made without sizing have a naturally high absorbency towards water due to the hydrophilic character of cellulose fibres. However, such papers may contain localised hydrophobic patches due to the presence of pulp-derived extractives, stickies and/or residual sizing species in recycled pulps. In such cases, the wetting by water can be improved by the addition of surfactants as absorbency aids, usually at quite low doses (<0.1% on fibre).

Absorption

This is a very general term for the incorporation of one material in another, eg for liquids or gases into solid materials. As absorption and adsorption are often difficult to distinguish from one another, the term sorption is used to cover both phenomena. The ability to absorb certain liquids, most commonly water, is relevant to some paper products and discussed under absorbency.

Accessibility

In papermaking, this term is encountered when discussing the interaction of polymers with particulate surfaces, notably with porous surfaces (like fibres) that can swell to varying degrees depending on local conditions. The fibre's pore structure (see swelling) imposes a maximum size on molecules that can gain access to the internal surfaces and this affects the extent of the adsorption of some (larger) polymers on the substrate (see representation below). This phenomenon is sometimes referred to as solute exclusion and is made use of in one of the techniques (fibre saturation point) for measuring fibre swelling. In real papermaking systems, this is a complex effect as the swelling of fibres and the size (molecular extension) of polymers are both affected by parameters such as the electrolyte content (conductivity) of the liquid phase.



The term "accessible" (or "non-accessible") is also applied when discussing the charged substances present in pulps. These are measured by titration with oppositely-charge species, the molecular size of which varies from tiny ions to quite large polymers. Titrations with small cations and polymers (eg Polybrene) can access all the charged organics to give the total charge, whereas larger polymers such as polydadmacs cannot, as they are too large to enter the pores. The charge value in the latter case is often referred to as the surface charge (for comparative values, see this table for various TCF pulps and this table for a range of mechanical and chemical pulps).

Acetic acid

This is a simple carboxylic acid (CH_3COOH) with a pK_A value of about 4.7 at 25°C. There are two distinct sources of acetic acid within papermaking systems:

- it is released from wood substances in Kraft and sulphite pulping processes and in the bleaching of mechanical pulps by the hydrolysis of acetyl groups (CH_3CO) on hemi-celluoses. It should not be present at significant levels in papermaking pulps due to its ease of removal in pulp washing.
- together with a number of other organic acids, it can be generated within the papermaking system by certain types of acid-producing bacteria. Concentrations of acetic acid up to several 1000 mg/l have been measured in waters on paper machines with closed water systems using recycled pulp. The main substrate (food source) for such reactions is dissolved starches.

Acid

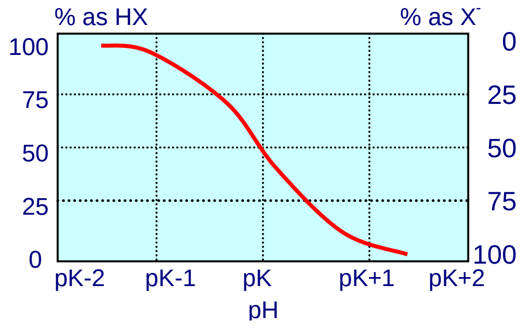
In contrast to a base, an acid is a proton donor through its ionisation reaction:

$$HX \rightarrow H^+ + X^-$$

the equilibrium constant, $K_A = c_H . c_X/c_{HX}$ or $pK_A = pH - \log (c_X/c_{HX})$

where c is the concentration (moles/litre) of the subscript species.

Strictly speaking, the above equation should use activities rather than concentrations. The best index of the strength of an acid is the pK_A value. When the ionisation of the acid is 50% complete (ie $c_X = c_{HX}$), pK_A = pH, ie the stronger the acid, the lower is its pK_A value (see ionisation curve at right). It can easily be shown that when the pH is more than about 1 unit above the pK_A value, over 90% of the species X (ie the sum of the concentrations of HX and X^-) is in the ionised form (X^-) and, conversely, when the pH is more than about 1 unit below the pK_A value, over 90% of the species labelled X above (ie the sum of the concentrations of HX and X^-) is in the unionised form (HX). This is illustrated for the hypohalous acids here.



One of the strongest acids is perchloric acid ($HClO_4$), which has a pK_A value of -7. Orthophosphoric acid (H_3PO_4) is much weaker and, having three protons, has three different pK values :

$$H_3PO_4 \leftrightarrow H^+ + H_2PO_4^- \leftrightarrow H^+ + HPO_4^{2-} \leftrightarrow H^+ + PO_4^{3-}$$

The pK_A value is about 2 for ionisation of its first proton, but the second proton ionises at a much higher pH (pK_A = 7) so the salt, sodium dihydrogen orthophosphate, gives a neutral solution and is therefore a useful buffer at around neutral pH. The third proton ionises at an even higher pH (pK_A = 13) so both disodium hydrogen orthophosphate and trisodium orthophosphate give alkaline solutions.

The above definition is sometimes called the Bronsted definition of acids, but there is an alternative definition when substances are referred to as Lewis acids. This concept originates from the fact that protons can be looked on as acceptors of electron pairs (as when they form hydroxonium ions with water) and bases as donors of electron pairs. This Lewis acid definition is mainly used in the context of metal ions.

In papermaking, acidic materials are used for a number of applications:

- alum for sizing with rosin, pitch control, etc, but it should not be used primarily for pH adjustment
- mineral acids such as sulphuric acid for pH adjustment
- machine system cleaning or fabric cleaning, which may use sulphuric or hydrochloric acids.

Acidic materials can also be generated in the papermaking system, notably through the action of micro-organisms, the most common examples being production of carbon dioxide and acetic acid. Acid papermaking is defined as where the wet end pH is below 6.

Acidity

Acidity is normally defined relative to the pH scale, where any value less than pH 7 (at 25°C) denotes an acidic condition, ie where the number of hydrogen ions (protons) exceeds the number of hydroxyl ions. Acidity is thus a measure of the concentration of protons or the quantity of alkali-neutralising substances in the system. Acidity is measured by titration with a standard alkali, normally to one of two end-points:

- titration to about pH 4.5, which is the pH where the traditional indicator methyl orange changes from red to yellow. This titration measures only strong acids, but the pH of most papermaking systems would be above this value.
- titration to about pH 9.2, which is the pH where the traditional indicator phenolphthalein changes from colourless to red. This titration will measure all free protons (ie the total acidity) and can also be utilised as a measure of the aluminium concentration.

Acid papermaking

Although there is no universally-accepted definition, acid papermaking can be defined as where the wet end pH is below 6. Although some papermaking additives may be somewhat acidic, the quantities used are usually insufficient on their own to increase the acidity below pH 6. However, if the last stage of the off-machine pulping or deinking process was acidic, the pulp might contain enough acid residues to generate an acidic stock. The actual papermaking pH obviously depends on the efficiency of the final pulp washing stage and on the presence of acid-neutralising materials in the stock (eg calcium carbonate filler and temporary water hardness). Acidic conditions can also be generated within the papermaking system through excessive microbial activity, but this would tend to be localised to within or close to slimes.

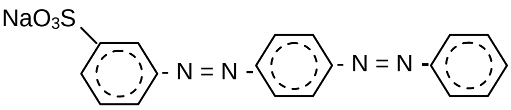
Where required, acid papermaking is managed positively through the addition of acidic materials such as sulphuric acid or alum. There are several reasons why an acidic papermaking environment is necessary, although this is much less common than it used to be:

- to optimise some aspect of paper quality such as
  - to create conditions in the sheet for a chemical additive to be effective, eg for sizing with rosin or for wet strength development with UF or MF resins
  - to prevent loss of brightness when using mechanical pulps
- to optimise some aspect of wet end operations such as
  - to maximise drainage
  - to minimise certain types of deposition such as from pitch.

Acid dye

This is the traditional term for the type of dye that can also be referred to as an anionic dye (although this term is best reserved for anionic direct dyes). In acid dyes, the chromogenic part of the molecule is the anion, the cation being either sodium or potassium ions. Acid dyes adsorb poorly on pulps as the chromogen contains negatively-charged sulphonate groups, which confer excellent water solubility, but poor adsorption, at least in the absence of alum or other cationic fixatives. Acid dyes are also usually small, non-planar molecules that cannot get close enough to the particulate matrix for non-electrostatic attractive forces such as hydrogen bonding or van der Waals forces to come into play.

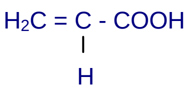
Most acidic dyes are based on derivatives of azo-compounds (see example at right), but the use of acid dyes now accounts for only 5% of the paper dye market and continues to decline due not only to poor retention, but also to poor fastness characteristics (particularly towards heat). The high solubility of acid dyes also limits their use for application at the size press, despite their having good chemical compatibility with typical size press chemicals, but they can be used at the coating stage due to their strong affinity for coating binders.



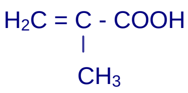
Acid yellow

Acrylates

This represents a group of chemicals used in the manufacture of various papermaking additives. They are all based on the unsaturated carboxylic acid, acrylic acid and its derivatives, the formulae of which are shown below.


$H_2C = \underset{\displaystyle H}{\underset{|}{C}} - COOH$

Acrylic acid


$H_2C = \underset{\displaystyle CH_3}{\underset{|}{C}} - COOH$

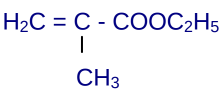
Methacrylic acid

$H_2C = C - C \equiv N$

Acrylonitrile

$CH_2 = CH - COOCH_3$

Methyl acrylate ester


$H_2C = \underset{\displaystyle CH_3}{\underset{|}{C}} - COOC_2H_5$

Ethyl methacrylate ester

The various types of acrylate used in papermaking are:

- polyacrylates used as dispersants, notably with coating pigments
- styrene-acrylate co-polymers used as coating binders
- styrene-acrylic acid co-polymers used for surface sizing
- anionic polyacrylamides used as retention and drainage aids
- acrylics with fluorinated groups as grease-resistant additives.

Activity

This term has a specific chemical meaning when discussing the solution properties of substances, notably electrolytes. The effective concentration of an electrolyte is less than its nominal mass concentration due to electrostatic interactions between the ions. In order to make an allowance for this and to define a substance's thermodynamic potential, the mass concentration (c) is replaced by its activity (a):

$a_i = \gamma_i . c_i$ where γ_i (gamma) is the activity coefficient of ion i

The activity coefficient can be estimated using various equations, but most are restricted to dilute solutions. The best-known is the Debye-Huckel limiting law, which should be applicable to most papermaking conditions in the following form:

$\log \gamma = \dfrac{-0.5\, z^2 .\, I^{0.5}}{1 + I^{0.5}}$ at 25°C where I = ionic strength and z = charge of the ion

For a divalent ion such as calcium, the activity coefficient could be as low as about 0.4 in the most concentrated papermaking system, but, in less extreme situations, should be no lower than about 0.7. For a monovalent ion such as sodium or bicarbonate, the effect is more moderate with the activity coefficient spanning the range 0.8-0.9 in most papermaking systems. The distinction between concentration and activity is important because it affects equilibrium constants such as solubility products and acid pK values.

Adhesion

This is the term for the strength of the attachment between dissimilar materials (as opposed to cohesion between similar materials) and can be derived from Young's equation:

Strength of adhesion between solid (S) and liquid (L) (mJ/m^2) = $\gamma_{LA} + \gamma_{SA} - \gamma_{LW} = \gamma_{LA}(1+\cos\theta)$

where γ_{LA} = interfacial energy between air/liquid (mJ/m^2)
and θ = contact angle between the solid/liquid

Not surprisingly, the adhesive strength is greatest when the contact angle is zero, ie the surface is fully-wetted by the liquid. To prevent adhesion or sticking therefore, the surface tension of the liquid needs to be minimised and the contact angle maximised (minimum wetting). In practice, the adhesive strength also depends on the smoothness/roughness of the surface and is greatest under ideal conditions where the surfaces allow 100% contact over their full contact area. Normally however, surfaces have a degree of roughness, which reduces the contact area so that the real adhesion is less than that calculated.

Adhesion is relevant to several phenomena in papermaking, some desirable and others undesirable:

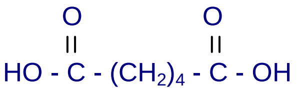
- places where good adhesion is required
  - between the base sheet and a coating layer
  - between the plys of multi-ply papers or boards
  - between the paper web and the surface of a Yankee/MG cylinder prior to possible creping.
  - in several paper applications such as printing and gluing.
- places where good adhesion causes problems
  - between wet end materials (usually the set of problematic substances like pitch, stickies, microbial slimes) and exposed surfaces leading to deposits and all their related problems

- between the paper web and surfaces on the paper machine (formation wires, press fabrics/rolls, dryer fabrics/cylinders, winders) leading to breaks and downtime
- between adjacent layers of the paper web on the winders and re-winders, these "stick-downs" leading to breaks and downtime.

Adhesion between surfaces makes an important contribution to the frictional characteristics of the paper web during manufacture and of the finished paper product. Release agents are chemicals added to the papermaking process to overcome adhesion problems or to enhance release properties in the product. Additives to enhance the creping of tissue products usually contain both release agents and adhesives. The latter also get into the papermaking system through their presence in recovered paper, notably packaging grades and are a major contributor to stickie problems.

Adipic acid

This is a dicarboxylic acid (see formula at right) that is used to make PAE resins and is sometimes incorporated in ASA size emulsions as a means of improving their stability.



$$HO - \overset{\overset{O}{\|}}{C} - (CH_2)_4 - \overset{\overset{O}{\|}}{C} - OH$$

Adsorbable organohalogens

These compounds (commonly abbreviated as AOX) became prominent in the late 1980s in the wake of the debate about the generation of halogenated (notably chlorinated) organic compounds when chemical pulps were bleached with chlorine gas. The term refers to the analytical technique used for their collective quantification, which relies on adsorption on activated carbon followed by coulometric titration of the halide ion. AOX measurement is used predominantly in the environmental field in relation to wastewater quality at bleached chemical pulp mills, but it has also been used in two areas of papermaking:

- to quantify the level of organohalogen compounds entering the papermaking system via the use of bleached chemical pulps and some papermaking chemicals such as PAE wet strength resins and some oxidised starches.
- to quantify the possible generation of AOX compounds through the use of chlorine-containing oxidants (eg chlorine dioxide and chlorine/bromine-release compounds) for control of microbiological problems.

Adsorption

This is the process whereby a substance accumulates at the interface between two phases, eg at the solid-liquid interface. As absorption and adsorption are often difficult to distinguish from one another, the term sorption can be used to cover both phenomena. Substances accumulate at an interface because this represents the most stable situation with the lowest free energy. The interaction leading to adsorption may result from chemical interactions, van der Waals attractions, electrostatic forces, hydrogen bonding or hydrophobic interactions.

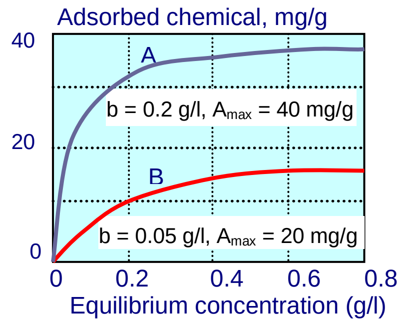
The key adsorption process in papermaking is the take-up of water-soluble substances by particulate surfaces (notably pulp and filler) at the wet end as this is the essential first stage by which all water-soluble wet end additives (eg starches, dyes, etc) are ultimately retained in the paper. As these adsorption processes are inherently complex, it is difficult to predict their precise outcome due to the non-accessibility of some surfaces and the polydispersity of both the adsorbing substance (the adsorbate) and the solid surface (the adsorbent).

Adsorption can be described by a number of quantitative models (Gibbs, Langmuir and Freundlich), most of which were developed originally for the gas:solid interface. The most commonly-used for papermaking systems is the Langmuir adsorption isotherm which assumes a monomolecular adsorption pattern and has the form:

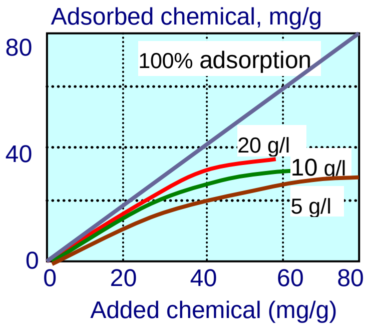
$$A = A_{max}.c/(b + c)$$

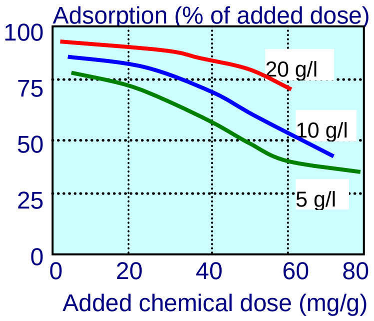
where A = adsorbed quantity of substance (adsorbate) per unit mass of adsorbent
A_{max} = maximum quantity adsorbed per unit mass of adsorbent
c = equilibrium concentration of substance remaining in solution
b = constant = equilibrium concentration when $A = A_{max}/2$

The Langmuir adsorption pattern is of the saturation type (see examples of various dose-response effects), where, simply due to space constraints on the adsorbent surface, there is always a maximum adsorption level (A_{max}) even at very high adsorbate doses. The b value, which is an indicator of the strength of attraction, varies widely as in the illustrated example at right, where substance A has a higher affinity for the surface than substance B and thus has a lower b concentration. An example of a substance with a high affinity for cellulosic surfaces is a cationic polymer, to the extent that it is sometimes difficult to detect any material in solution at low polymer doses (see this figure for several cationic starches).



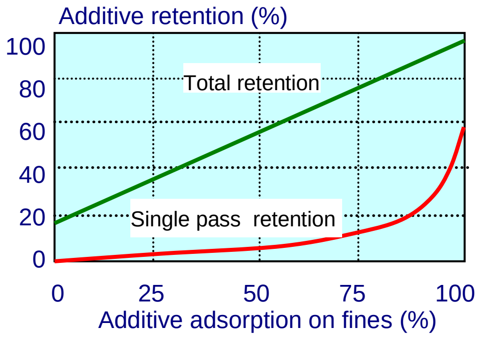
In some cases, it is useful to look at adsorption in terms of the adsorbed quantity versus the amount of substance added and this calculation also involves the concentration of the adsorbate. This can be plotted in two forms - the adsorbed quantity versus the dose at different adsorbent levels (as shown in the figure at left below, which is often how dose-response effects are judged) or as the adsorption efficiency versus the dose at different adsorbent levels (as shown in the figure at right below). It is clear, that, although the quantity adsorbed is greatest at high adsorbate doses, this is achieved at the expense of impaired overall efficiency. The data also shows that the highest efficiency is achieved at the highest adsorbent concentration, eg at a dose of 20 mg/g (2% dose on solids), the efficiency increases from about 70% at 5 g/l to about 90% at 20 g/l adsorbent concentrations





This suggests that addition to the thick stock should give the best overall additive retention. However, for additives with a range of molecular weights (as is the norm for papermaking polymers), the plot of adsorption versus equilibrium concentration may also depend on adsorbent concentration as the polymer fractions are not uniformly adsorbed across the molecular weight range. This can lead to better overall adsorption (and retention) at lower adsorbent concentrations. Dilution of a suspension with adsorbed material may also lead to desorption of the adsorbate unless the process is irreversible.

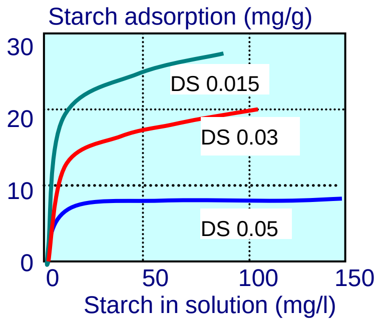
The retention of a water-soluble wet end additive is critically dependent on its adsorption on the particulate matrix, as illustrated in the figure at right below using the standard model of the papermaking wet end. This example assumes that the additive adsorbs only on the fines fraction, which has a single pass retention of 60%. It is clear that the single pass retention of the additive declines very rapidly (from 60% when it is all adsorbed on the fines) as the adsorption falls below 100%, ultimately reaching the same, very low level (at 0% adsorption) as the dissolved solids. The additive's total retention declines more steadily as adsorption decreases, but, given the significant price of most additives, it is still necessary to achieve at least 80% (and preferably even higher) adsorption. It is also possible to model the effect of water closure on additive retentions and this is shown here (fresh water use in the above example is 10 m^3/tonne in the main papermaking circuit).



As adsorption is the key to cost-effective use of water-soluble wet end chemicals, it is important to know the main factors that influence this parameter. In most cases, the extent of wet end adsorption depends on two key factors:

- charge difference between adsorbent and adsorbate

  This is the main mechanism used to promote adsorption and, as papermaking surfaces are generally negatively-charged, this means the use of cationic additives. One of the factors that then determines the amount of the additive that can be adsorbed is the total charge on the particle surface against the total charge from that dose of additive. As illustrated at right for starches of varying cationicity on the same bleached Kraft pulp, the maximum adsorption increases as the starch cationicity is lowered in order to maintain a balanced surface:additive charge ratio. However, in this particular case (and many others), the total charge of the adsorbed starch is always less than the total pulp charge because of accessibility constraints.

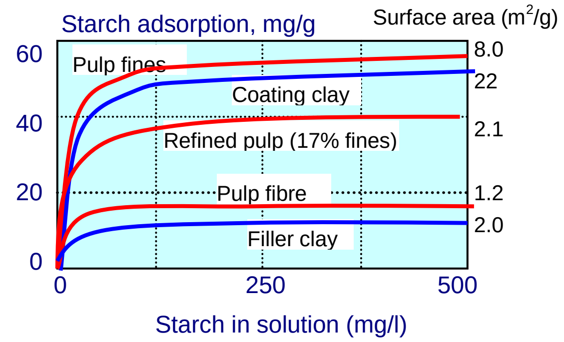


Source: Wagberg, Nordic Pulp Paper Research J., 1993, 4, 399-404.

  It should be noted that the maximum wet end adsorption is not always achieved with cationic additives as certain conditions (such as high dissolved calcium levels) may be better suited to anionic additives (see anionic starch). In other situations, the additive may only be available with a certain cationic charge density, which might limits its adsorption below the desired level. In this case, it may be beneficial to use a charge-balancing anionic additive with the cationic polymer, a good example being the use of anionic polymers (such as CMC) with PAE wet strength resins.

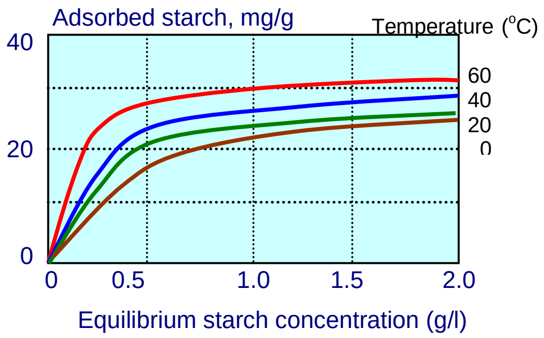
- the adsorbent's surface area

  The surface area of the adsorbent depends mainly on its particle size, but also on its shape, there being an order of magnitude difference in the specific surface area of the larger particles (intact fibres) and fines (see this table). For fibre surfaces, adsorption also depends on the accessibility of internal pore surfaces to polymers depending on the latter's molecular size. Both the swollen state of fibres and the conformation of polymers are influenced by the same parameters (eg electrolyte levels), but the adsorbed conformation/size may be different to its conformation/size in solution. As shown at left for a cationic starch, adsorption is related to surface area (although not necessarily in an obvious linear fashion) for various forms of the same mixed hardwood-softwood bleached Kraft pulp and for two different clays.



Source: Marton in Tappi J., 1980, 64, 7, 87-91.

Temperature is another important wet end variable, but its influence on adsorption processes is less clear-cut. To be favoured thermodynamically (ie negative free energy change), the adsorption process has to be exothermic in order to compensate for the expected loss of entropy that all polymers experience on adsorption. Data for the adsorption of a cationic starch on a bleached chemical pulp at about pH 4 (shown at right) suggests otherwise as adsorption increases with temperature, indicating an endothermic process that has to be balanced by an increased entropy of the total system.



Source: Nedelcheva in JCIS, 1978, 66, 3, 475-482.

Aerobic

This word simply means in the presence of oxygen and is mainly relevant to the microbiology of the papermaking process. The maintenance of aerobic conditions in the papermaking system is desirable as the development of anaerobic conditions is thus prevented or at least minimised. In the presence of other essential nutrients, aerobic conditions do, of course, allow aerobic bacteria to grow with all their attendant problems and control of such growth is thus an important aspect of microbiological control.

Affinity

This term is mainly used in colour chemistry in relation to the ability of dyes and fluorescent brighteners to remain associated with the substrate when rewetted, ie good fastness against liquids.

Aggregation

This term is applied to the natural or chemically-induced association of particles into larger structures, which is one of the main objectives in wet end chemistry. In particular, it is a useful term for describing this bringing together of fine particles as it does not imply the involvement of any particular mechanism, as do the alternative coagulation and flocculation terms.

AKD

This is an abbreviation for the sizing agent alkyl ketene dimer.

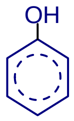
Alcohols

Alcohols are organic chemicals with only a hydroxyl group attached to the carbon atom (formulae at right below). They are little used in papermaking as such, but are used to make certain papermaking chemicals such as those with ester groups. Methanol is released from cleavage of methoxy (-OCH_3) groups in lignin during Kraft pulping, but being volatile, little if any remains with the pulp. Lignin itself is a polymer based on substituted phenolic units. Alcohols such as iso-propanol (see formula at right) may be present in dye formulations to improve solution stability and can be used as solvents for some surface-applied chemicals (eg silicones). They are also widely-used in some printing processes.

R - OH where CH_3OH is methanol

C_2H_5OH is ethanol

$(CH_3)_2CHOH$ is iso-propanol


is phenol

There are three different sorts of alcohol depending on the bonding of the OH-attached carbon:

- primary alcohols are where the hydroxyl-bonded carbon atom is bonded to only one other carbon atom (as in methanol and ethanol)
- secondary alcohols are where the OH-attached carbon atom is bonded to two carbon atoms (as in iso-propanol)
- tertiary alcohols are where the OH-attached carbon atom is bonded to three carbon atoms.

All the above are mono-hydric alcohols. Chemicals having two hydroxyl groups (di-hydric alcohols) are called glycols, which are used to make some polymers used in papermaking. A poly-hydric alcohol, sorbitol, is used as a humectant in some papers. A tri-hydric alcohol, glycerol, is used to make rosin esters and some fatty acids in the extractives fraction of wood are present as triglyceride esters.

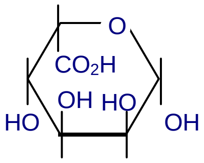
Aldehydes

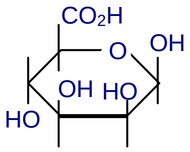
Aldehydes are organic compounds containing the H - C = O group and are formed by the oxidation of primary alcohols. This group is present in some papermaking chemicals:

- the simplest aldehyde, formaldehyde (HCHO) is used to make UF resins, UF pigments and MF resins
- the dialdehyde glyoxal is used as an insolubiliser in coatings and is also used to make polyacrylamide-based wet strength agents
- the dialdehyde gluteraldehyde is used as a biocide
- dialdehyde-starches that can give temporary wet strength
- the open chain, non-cyclic form of monosaccharides such as glucose has a terminal aldehyde group, which accounts for their reducing properties.

Alginates

Alginates are salts of alginic acid, which is a polyuronide of two hexuronic acids, β - D - mannuronic acid (far right) and α - L - guluronic acid (near right). Alginates are obtained from brown seaweed and are used in paper coatings as thickeners and water retention agents.





Alkali

An alkali is an alternative name for a base.

Alkalinity

This is normally defined relative to the pH scale, where any value above pH 7 (at 25^{o}C) denotes an alkaline condition, ie where the number of hydroxyl ions exceeds the number of hydrogen ions (protons). Alkalinity is thus a measure of the concentration of hydroxyl ions or the quantity of acid-neutralising substances in the system. It is not linearly related to pH as some substances have an acid-neutralising buffer capacity, but do not dissociate to give high levels of hydroxyl ions. The best examples in papermaking are carbonate (as in calcium carbonate fillers) and dissolved bicarbonate ions. Alkalinity is measured by titration with a standard acid, normally to one of two end-points:

- titration to about pH 9.2, which is the pH where the traditional indicator phenolphthalein changes from red on the alkaline side to colourless on the acid side. This titration measures all free hydroxyl ions. Most papermaking systems are already below this pH, indicating that significant levels of free hydroxyl ions are absent.
- titration to about pH 4.5, which is the pH where the traditional indicator methyl orange changes from yellow on the alkaline side to red on the acid side. This titration measures free hydroxyl ions plus weaker bases such as bicarbonate and is often referred to as the total alkalinity.

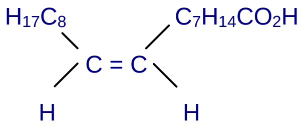
The dissolved alkalinity is not a conservative parameter, so the measured level on a paper machine depends not only on the input of alkaline substances and the degree of water closure, but also on interactions within the system. Some values are shown here for several machines with fully-closed water systems.

Alkaline papermaking

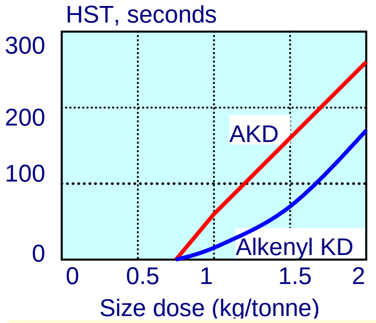
Although there is no universally-accepted definition, alkaline papermaking can be defined as where the wet end pH is above 8. Although some papermaking additives may be somewhat alkaline, the quantities used are usually insufficient to enter the alkaline papermaking region. The exception is the addition of calcium carbonate filler, which can take the alkalinity into the range pH 8-8.5, but this is not common. There is perhaps only one reason for positively managing an alkaline wet end pH, which is to enhance the efficiency of AKD sizes through the addition of, for example, sodium carbonate.

Alkenyl ketene dimer

This is a variant of the standard alkyl ketene dimer size, but is based on unsaturated, instead of saturated, fatty acids. The unsaturated acids are typically the mono-unsaturated oleic acid (see structure at right) or the di-unsaturated linoleic acid. The cis-isomer structure of oleic acid gives the hydrocarbon chain a bent configuration, which means that the molecules cannot pack together as closely as the linear saturated AKDs. Consequently, the alkenyl KD and its corresponding ketone are liquids at ambient temperature.



The development of these ketene dimers was driven by problems experienced with some AKD-sized papers during printing. These problems (eg poor register, jamming, sheet billowing) were attributed to the presence of AKD and/or its ketone hydrolysis product, which gave the surface a low friction coefficient making it very slippy. Laboratory and commercial tests have clearly demonstrated that the alkenyl ketene dimers give much better runnability as they are not able to form solid deposits. However, their sizing ability is not as good as normal AKDs as indicated at left in terms of the HST value. This is attributed to the more compact molecular structure, which gives smaller surface coverage at the same retained size level. Other work has indicated that there may also be a retention component in the difference in sizing efficiencies and that the liquid alkenyl KDs show better sizing at lower drying temperatures due to their ease of re-distribution. Adhesion to drying cylinders is also better than with AKD-sized papers so glaze is improved for MG papers.



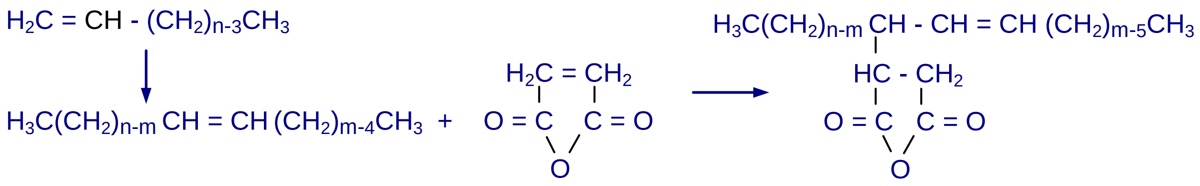
Source: Brungardt in Proceedings Tappi Papermakers Conference 1996, 297-308.

More recent work in Japan has investigated the size reversion of alkenyl KD-sized papers using an accelerated ageing procedure in which the papers are exposed to air blowing and uv irradiation. This has shown that papers sized with alkenyl KD lose more of their sizing than do AKD-sized papers and that this is aggravated by the presence of PCC filler. This has been attributed to auto-oxidation of the alkene group with atmospheric oxygen leading to a less hydrophobic molecule. This mechanism is similar to that proposed for the size reversion of ASA-sized papers.

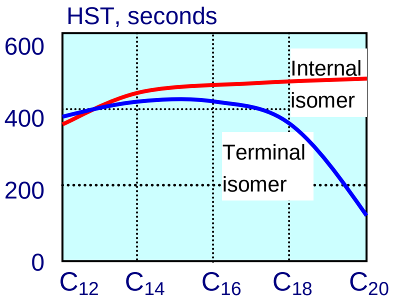
Alkenyl succinic anhydride (ASA)

ASA is a wet end sizing agent that, like AKD sizes, is effective at neutral pH, but ASA began to be used as a papermaking size somewhat later, mainly during the 1970s. The size is manufactured by reacting a petroleum fraction containing a mixture of alkenes with maleic anhydride (the same chemical used to produce fortified rosin size). If the natural alkenes with a terminal double bond (1-alkenes or α-olefins) were used, the product would be a waxy solid that would be less easily emulsifiable than if the ASA were in a liquid form. Consequently, the natural alkenes are isomerised catalytically beforehand to produce a mixture of alkenes with the double bond in different (internal) positions. This modification does not allow the ASA molecules to pack together as closely and the product is thus an oil rather than a wax.

The reaction scheme is shown below, noting that the position of the double bond in the alkenyl chain is shifted along by one position in ASA:



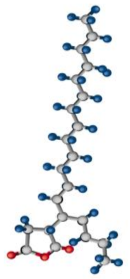
The name succinic anhydride comes from the name for hydrogenated maleic anhydride (no alkene linkage), which is the form in the ASA molecule. The total length of the alkenyl chain (n in the above reactions) is in the range 15 to 20, the most common chain length in commercial products being 16 and 18, which is a compromise between sizing efficiency and ease of emulsification (ie the ability to prepare a uniform emulsion without the need to liquefy the alkene by heating, which would promote hydrolysis).

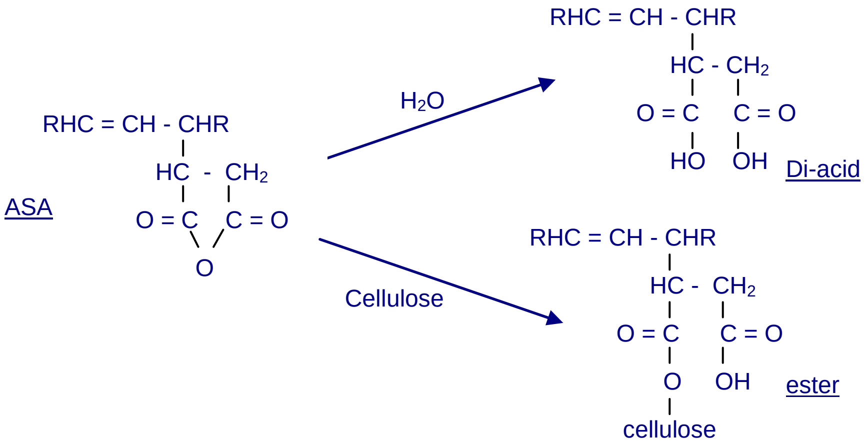


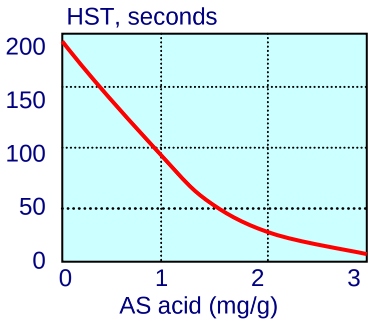
Source: Roberts at Pira Conference "Chemistry of Papermaking", 1993.

An example of the effect of double bond position and alkenyl chain length on sizing efficiency is shown in the figure above at right, although in this case the ASA was added in a toluene solution to the pre-formed paper rather than by wet end addition. Another factor in the selection of starting materials is the potential vaporisation of the ASA during drying and it has been found that the higher alkene (C_{18}) is better in this respect (less vaporisation) simply due to its higher molecular weight. Recent molecular modelling of the conformation of ASA molecules has confirmed the superiority of the internal alkenyl structures from a theoretical viewpoint and that the C_{18} chain length gives the highest surface coverage on cellulose fibres.

The reaction chemistry of ASA (shown below) has similarities with that of AKD in terms of its potential reactions with both water and cellulose. However, ASA is much more reactive than AKD and is not therefore sold as a ready-to-use emulsion, but the emulsion is always prepared on-site. Exceptions to this are the water-in-oil ASA emulsions, which simply need inverting with water before use and the saponified ASA sizes used mainly in Japan.







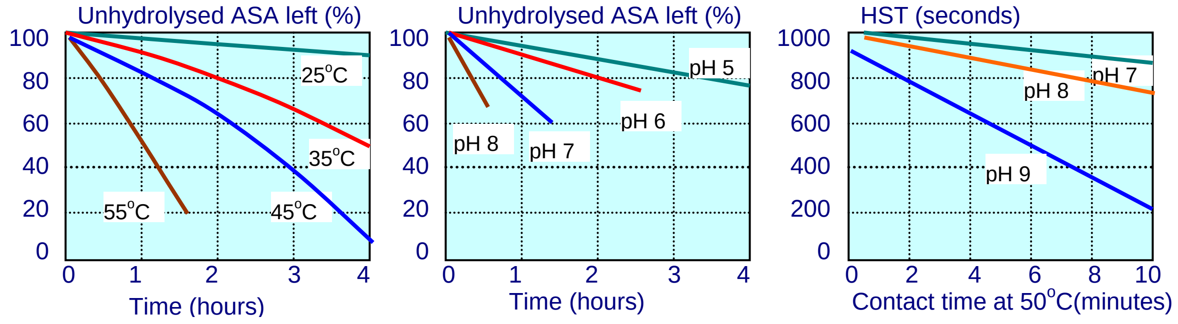
Source:Roberts in Proceedings 10th Cellulose Conference, Syracuse, 1988.

Having selected an ASA with a certain alkenyl group, the next consideration is the purity of the ASA product for on-site emulsification. A high purity is very important due to the known adverse effect of ASAs with high levels of the di-acid, which has been shown not only to have no sizing activity, but also to be a de-sizing agent. In the example at right, the AS acid was added to an ASA-sized paper in toluene solution and a clear loss of sizing is evident. Solvent extraction to remove the AS acid restored the sizing to the original level (about 200 seconds HST). In another case reported, purification of a raw ASA by distillation doubled its sizing efficiency.

The quality of the on-site produced emulsion is one of the important practical variables determining ASA's overall performance and emulsification is usually carried out with proprietary equipment provided by the size supplier. These systems vary in terms of the chemical(s) used for emulsification and the level of mechanical agitation employed during emulsification. Additional chemicals may be used such as stabilisers to inhibit particle coalescence, promoters to induce hetero-flocculation with fibres and activators to facilitate efficient emulsification. The disadvantage of the low-shear emulsification systems is that much higher levels of surfactant-based activators are required (up to 5% compared to no more than 1% in high-shear systems) and this may be detrimental to sizing.

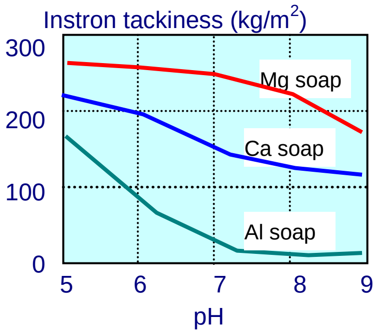
The optimum overall particle size of the emulsion is a compromise between "large" particles for good retention by filtration through the mat and minimisation of hydrolysis (but possible agglomeration and deposition) against "small" particles for a uniform distribution across the fibres and high retention by hetero-flocculation with the rest of the particulate matrix. Optimum particle size is normally considered to be 1-2 microns. The traditional chemical that acts as a promoter and stabiliser is cationic starch, but synthetic cationic polymers are also used for this purpose. The normal ratio of starch:ASA is about 2:1, but ASA sizing efficiency continues to increase up to a 5:1 ratio due to the stabilising effect of starch on emulsion particle size. From various studies, the impact of the degree of starch cationicity on sizing efficiency is unclear and this is most likely explained by differences in pulp anionicity. Charge optimisation, not just of the starch but of other charged additives, would need to be carried out in each individual situation. Many paper machines making sized papers would be using wet end starch for dry strength and any starch added with ASA should be available for dry strengthening the paper once it is released from its emulsification role. Whilst little effect of starch molecular weight has been observed in relation to ASA sizing performance, this would be still important in relation to its dry strengthening.

Following preparation in this form, the fresh size should be dosed directly to the moving thick stock just prior to the fan pump or to the thin stock in order to minimise contact time and hydrolysis. Although the emulsion is made cationic to maximise association with the rest of the particulate matrix, retention aids are essential to achieve high single pass fines/ASA retentions and thus limit wet end hydrolysis. Wet end hydrolysis generates the AS di-acid (as seen in the above reaction scheme) and the extent of this reaction varies with both wet end temperature and pH as shown in the examples below. The picture at right below shows the effect of hydrolysis on sizing performance in the presence of 15% calcium carbonate filler. Although there is a significant reduction in sizing, the paper is still reasonably sized, even after 10 minutes at pH9 and 50°C. The addition of adipic acid to the emulsion has been found to stabilise the pH and slow the hydrolysis rate.



Source: Wasser in Proceedings 1985 Tappi Alkaline Papermaking Seminar, 17-20.

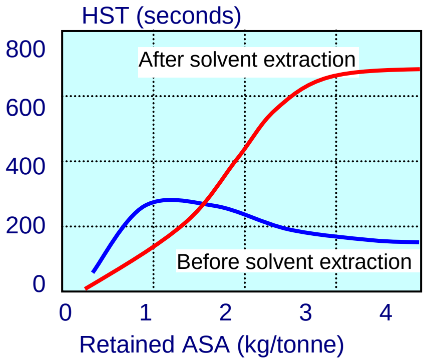
The di-acid hydrolysis product can react with any cations available to form the soap, calcium being the most prevalent ion in most papermaking systems that use ASA size at neutral pH. As shown in the figure at right, the calcium soap is quite tacky (although less so than the magnesium soap), but the aluminium soap is relatively tack-free, at least in the neutral pH range. The addition of alum (or other aluminium salts) to ASA-sized systems has generally been shown to be beneficial to its sizing performance. This is likely to be due to the "normal" ability of alum, even at neutral pH, to neutralise any anionic trash present plus the precipitation of the di-acid in the soap form. This is confirmed by the fact that the most effective alum regime with ASA is a total dose of about 0.5% split between addition of most to the machine chest before ASA dosing and the rest as a small trim dose to the thin stock. It has also been found that the use of chlorine dioxide as an on-machine biocide can detackify calcium soaps of ASA. Retention of the hydrolysate in the paper does not cause a slippy surface (as in the case of AKD), but press picking can be severe for the calcium soap and, most importantly, the free acid can act as a desizing agent.



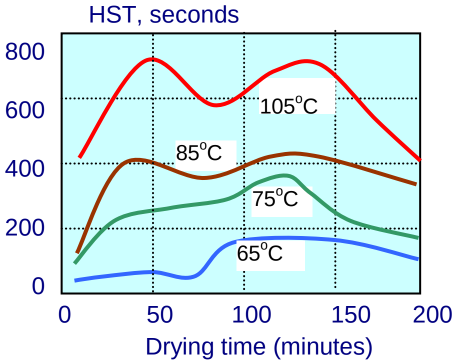
Source: Proverb in Proceedings 1989 Tappi Papermakers Conference, 91-96.

Some work has been carried out on the effects of dissolved calcium and bicarbonate on sizing efficiency rather than just on the hydrolysis aspect. High calcium levels (2 g/l) do negate sizing compared to a more typical calcium level (0.2 g/l) - this could be an ASA retention-related effect due to its blocking of anionic sites on the pulp or a hydrolysate-related effect. Bicarbonate has very little effect at levels up to 2 g/l.

Once retained in the sheet, sizing develops more rapidly than with AKD sizes and there are usually no problems from inadequate cure at the size press or at the final reel. Due to their high reactivity, there had never been any doubt about the mechanism of ASA sizing being one of direct ester formation with cellulose, which has been demonstrated using FT-IR. As with rosin and AKD, research using ^{14}C-labelled size has shed some light on the factors affecting ASA cure and sizing development. Removal of "non-reacted" ASA by solvent extraction shows the adverse effect of retained hydrolysate on sizing (see figure below at left). Even though it is more reactive, sizing with ASA is, like AKD, also accelerated by raised temperature (see figure at right below).

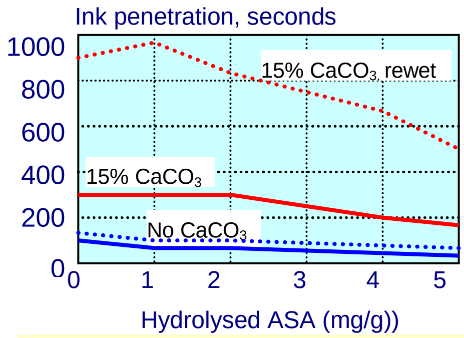


Source: Roberts in Proceedings 10TH Cellulose Conference, Syracuse, 1988.



Source: McCarthy and Stratton, Tappi J., 1987, 70, 1, 117-121.

Other than its identification as a tacky precipitate at the wet end, there has been very little work carried out on the effect of the calcium soap of the AS acid once it is in the paper. The data in the figure at left shows the effect of rewetting (with deionised water) an ASA-sized paper (with and without calcium carbonate filler) with various added levels of the hydrolysate. The sizing level of the unfilled paper declined with increased hydrolysate content and rewetting had no effect. The sizing level of the filled paper also declined with increased hydrolysate content, but showed a remarkable improvement on rewetting (including the case with no added hydrolysate). This effect is attributed to the in situ formation of the calcium salt of the ASA acid on rewetting. This suggests improved sizing when ASA-sized papers are further treated at the size press.



Source: Proverb, Tappi J., 1998, 81, 7, 139-146.

Since its introduction in the 1970s, the uptake of ASA as a wet end size has been slower and less uniform than AKD. Its most consistent market has been the sizing of plasterboard, but this has as much to do with deficiencies of rosin and AKD as it has to do with the performance of ASA. This grade is largely made with recycled pulp, in which the presence of calcium carbonate dictates neutral sizing, but which can be difficult with rosin. The problem with AKD has nothing to do with its sizing per sec, but the fact that AKD-sized surface cannot bond adequately with the plaster layer. ASA is also widely-used to size wood-free fine papers although there are large regional differences in its uptake, ASA use generally being stronger in North America.

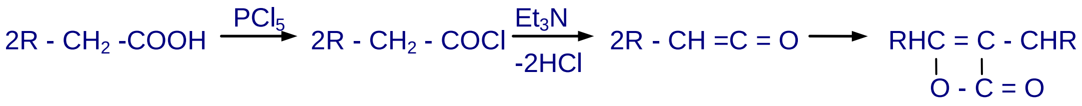
The other main sizing sector (packaging boards such as linerboard) is generally still sized with rosin or AKD, although some recycled machines do size with ASA due to problems of slow cure and low friction coefficient with AKD. Various studies with ASA have shown that it does not produce a slippy surface. Addition rates for ASA are 1-4 kg/tonne paper with doses for wood-free fine papers being at the low end and for plasterboard at the high end of this range. Where cationic starch is used for emulsification, addition rates are typically double the ASA dose, a range that happens to cover the normal span of addition rates for cationic starch as a dry strength additive.

Alkyl ketene dimer (AKD)

AKD sizing agents sizes were developed in the 1950s and were initially marketed, predominantly for surface application, as a powder product with pre-mixed nonionic emulsifier. For wet end addition, a cationic product is preferable in order to aid aggregation with the rest of the particulate matrix and this led to the original liquid AKD sizes emulsified with cationic starch to give a total solids content of about 7.5%. At this time, they were often used in combination with separate addition of a polyamide-epichlorhydrin (PAE) resin as a retention/cure promoter. The great advantage of these sizes was their ability to size under neutral pH conditions with a useful additional benefit being that the sized paper also gave some resistance to acidic and alkaline fluids. At that time, rosin was the most widely-used wet end size, but this required acid papermaking conditions (typically pH 4.5-5 at the time) for effective sizing. Today, AKD is the most widely-used wet end sizing agent, but the formulation often incorporates other polymers (in addition to emulsifiers) to aid retention/cure and total solids contents can go up to about 30%. AKD is also used at the size press, but this is usually in an anionic form in order to be compatible with other chemicals present.

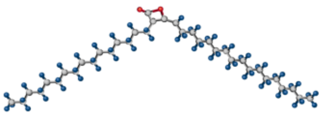
AKDs are made from fatty acids, such as palmitic and stearic acids, derived from hydrogenated tallow. This length of hydrocarbon chain has been shown to be about optimum in terms of overall sizing efficiency and this source is also a cost-effective starting material. However, it should be noted that other factors may dictate a different blend of fatty acids, one of the issues being the wet end deposition tendency, which has been shown to be worst when the melting point of the AKD is about the same as the temperature of the wet end stock.

Phosphorous pentachloride is used to convert the acid to the acid chloride, which is then dehydrochlorinated with triethylamine to form the alkyl ketene monomer. This dimerises to yield AKD, which has the form of an internal ester known as a β-lactone. The use of palmitic and stearic acids lead to the tetradecyl and hexadecyl ketene dimers respectively. The overall reaction scheme is as follows:

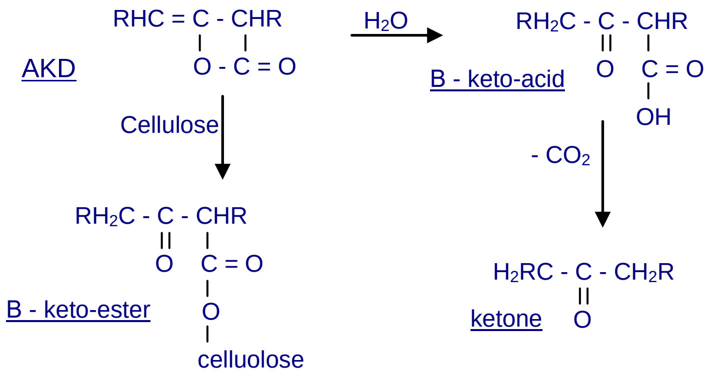


$$2R-CH_2-COOH \xrightarrow{PCl_5} 2R-CH_2-COCl \xrightarrow[-2HCl]{Et_3N} 2R-CH=C=O \longrightarrow \begin{array}{ccccc} RHC & = & C & - & CHR \\ | & & | & & \\ O & - & C & = & O \end{array}$$

In order to optimise the reaction conditions, toluene is added at low levels (1000-5000 ppm) and can remain in the AKD wax after evaporation and this can be retained in the paper along with the AKD. The manufacturing process can be modified either to lower the toluene level (to 10-100 ppm) or to eliminate its use altogether to produce a toluene-free AKD. This is particularly important for AKD-sized papers used for food contact. AKD wax has an interfacial energy with air of about 33 mN/m at 20°C, reducing to about 27 mN/m in the liquid state at 75°C.



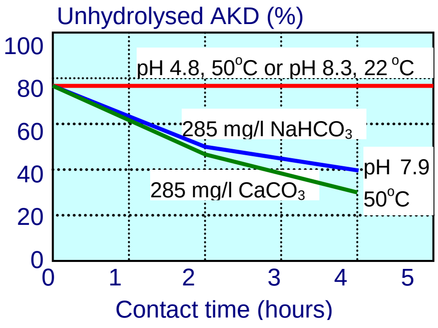
As is evident from its formula, the β - lactone ring provides the hydrophilic centre of AKD to which are attached the hydrophobic alkyl groups (see representation at right), which makes it a more extended molecule than rosin. These are the most commonly-used AKDs and are light brown, waxy solids with melting points of 40-60°C. AKDs based on unsaturated acids (eg oleic) or branched saturated fatty acids (eg isostearic) are oils at normal ambient temperatures as their molecules cannot pack together that closely due to steric factors. The alkenyl ketene dimers based on oleic acid began to be used as sizing agents for paper in the mid-1990s in order to overcome some problems associated with papers made using the normal AKDs.



AKD sizes are sometimes called reactive sizes due to their claimed chemical reaction with cellulose to form a β-keto-ester (see diagram at left). AKD can hydrolyse by opening of the lactone ring to generate the β-keto-acid, which then rapidly decarboxylates to the dialkyl ketone under alkaline conditions.

This relatively simple reaction scheme is complicated by the fact that the hydrolysis reaction with water may take place at various locations in the papermaking system (the stored emulsion, the wet end stock and the sheet at various stages of drying), whereas the reaction with cellulose is only likely to take place during drying. Given that there is likely to be a difference in the sizing efficiency between the various AKD entities (intact AKD, the β-keto-acid, the β-keto-ester and the ketone), it is not that surprising that that there has been (and still is) significant disagreement about their relative contributions to the sizing of paper. However, it is generally agreed that hydrolysis, at least at any time before the final drying stage, is undesirable for two main reasons:

- ❑ hydrolysis products in the emulsion (due perhaps to over-long storage at high ambient temperatures) can lead to deterioration in emulsion quality and impaired dispersability in the papermaking stock.
- ❑ hydrolysis products at the wet end may contribute to wet end deposition problems and deposition/picking during later pressing and drying.

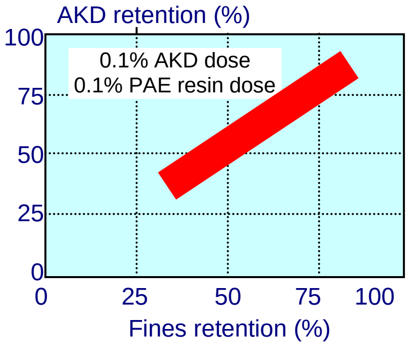


Source: Jiang in J.Pulp Paper Research, 2000, 26, 6, 208-213.

Hydrolysis in the supplied emulsion is minimised by maintaining the pH at about 3 and by storage at the lowest practical (above freezing) temperature. Incorporation of cure promoters (such as PAE resins) within the emulsion accelerates the wet end hydrolysis rate as well as the cure rate. The hydrolysis rate under neutral pH conditions has been shown to be much slower than the cure rate, but it increases more rapidly (than the cure rate) with rising temperature so is likely to be a more significant effect during sheet drying. Other wet end parameters influence the hydrolysis rate as shown for some selected conditions in the figure at left where the course of hydrolysis was followed for a diluted AKD emulsion (100 mg/l concentration). This confirms the stability at low pH and low temperature, but indicates considerable hydrolysis in the presence of sodium bicarbonate and calcium carbonate (as will be shown later, the same type of substances that also enhance the rate of AKD cure). This same study also showed that neutral electrolytes (NaCl, $CaCl_2$) had little impact on hydrolysis at higher concentrations (1-3 g/l).

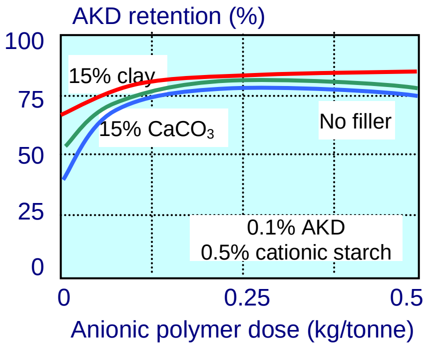
As with other wet end sizes, the first critical step with AKD is to achieve a uniform distribution within the particulate matrix followed by a high single pass retention on the wire. The retention aspect is more important than with rosin due to the increased hydrolysis of AKD if it is recycled many times in the whitewater before finally being retained. There is very little data available on AKD retention on actual paper machines due to the difficulties of chemical analysis.

However, laboratory work has been carried out with radio-active (^{14}C) labelled AKDs, which provides an insight into the variables affecting AKD performance. As a fine particle emulsion (typically 0.5-1μ), the AKD size is retained by a hetero-flocculation mechanism with the rest of the particulate matrix. As a cationic particle, the AKD should have some electrostatic attraction with the anionic fibre fines/fillers and it has been shown that there is usually a good correlation between fines retention on the wire and AKD retention (see figure at right for a wide range of data from various experiments using pulp only and pulp + fillers with and without an anionic polyacrylamide retention aid).

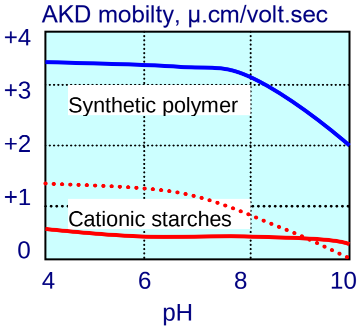


Source: Davison in Proceedings Tappi 1985 Alkaline Papermaking Conference

These results were corroborated in a separate study using the dynamic drainage jar, in which it was shown that a minor, but significant, AKD fraction (20-30%) was associated with the pulp's fibre fraction. However, the overall AKD balance was determined by the relative surface areas of the whole particulate matrix (pulp fibre, pulp fines and filler). Another study has shown that the anionicity of the pulp influences the retention of AKD, thus again confirming AKD's retention mechanism as being a charge-mediated hetero-aggregation with the whole of the particulate matrix (like that of filler particles). When the anionic charge on the fibre is blocked chemically, a higher AKD dose is required to bring about sizing. This is consistent with the observation that pulps with a naturally low anionic content (eg bleached chemical pulps based on some non-wood fibres like cotton) are more difficult to size than normal bleached Kraft wood pulps.



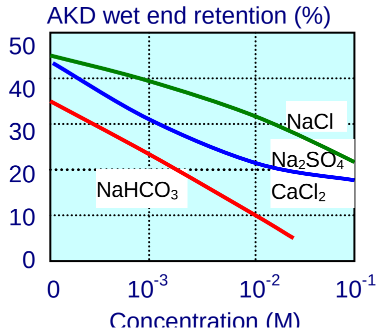
Further data from the above-quoted study (at left, but with AKD plus cationic starch rather than PAE resin) indicates how one particular retention aid affects AKD retention with and without added filler. It is not sensible to generalise too much about the best retention aid systems for AKDs (as this depends also on other additives present), but it has often been found that anionic polyacrylamides are very effective (as seen here). However, many different retention aid systems are employed on AKD-sized machines and the universal key issue is the need for good fines retention, which should ensure good AKD retention. Sizing data from wood-free fine paper machines using AKD is given here for an uncoated machine and here for a coated machine.



Source: Esser in Proceedings 1997 FRS "Fundamentals of papermaking materials"

There have been conflicting results on the effect of wet end pH on AKD retention, which is not surprising in view of the range of chemicals that may be present in the AKD emulsion. However, over the normal operating pH range for AKD sizes (pH 7-8.5), there should not be that much impact on its single pass retention. This is evident from the figure at right for two different AKD emulsions, one prepared with a weakly cationic starch and one with a much more cationic synthetic polymer (both having quaternary nitrogens). The more cationic of the two starches (data from a different study) was prepared from a cationising chemical having tertiary nitrogens, so, despite having a higher nitrogen content, the starch lost its cationicity at alkaline pH. At most mills using AKD size, the wet end pH is not actively controlled, but is allowed to buffer at the natural pH dictated by the bicarbonate/carbonate equilibria. The exceptions are those mills adding extra alkalinity to boost the AKD cure rate (see later in this section), in which case the pH may be lifted above pH 8 (see this example of chemistry data from AKD-sized machine using sodium carbonate as a size promoter).

Other wet end additives can influence AKD retention significantly. Although alum (or PAC) is not needed to achieve sizing with AKD, it is still sometimes used as part of retention aid systems or to control anionic trash. Again, there have been some conflicting results published, but low alum/PAC doses (<0.5% on fibre) should have no significant deleterious effect and could be beneficial when anionic trash is present. Anionic substances such as lignosulphonates have been shown capable of impairing AKD retention through reducing the cationicity of the emulsion. It is thus not uncommon to use cationic additives as a separate component with cationic AKD sizes as was standard practice (in the form of PAE resins) when they were first introduced. As shown in the figure at right, electrolytes have an adverse effect on AKD retention due to shielding of the electrostatic attraction between the cationic size and anionic fibre, but this can be overcome through the use of normal retention aids.



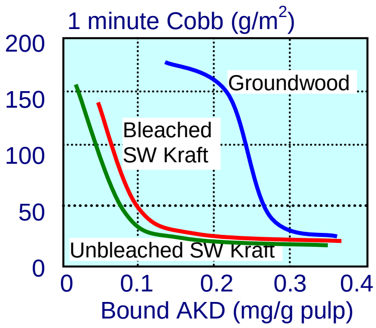
Source: Lindstrom et al in Nordic Pulp Paper Res.J., 1986, 2, 31-45.

Although good retention allied to a uniform distribution within the particulate matrix is a pre-requisite for effective AKD sizing, this is dependent on wet end factors that are similar to those relevant to other functional cationic additives. AKD emulsions are most commonly added in an undiluted form close to the fan pump, often just on the thick stock side, as this gives good mixing with the particulate matrix. This addition point also gives a reasonably low contact time and thus minimises any hydrolysis tendency, this factor being of most importance at higher stock temperatures (>40^{o}C).

The most controversial (and fascinating) aspect of AKD sizing relates not to its wet end chemistry, but to its dry end chemistry, notably its sizing mechanism once it is present in the paper web. The main question is whether the AKD does react with cellulose to form the β-keto-ester, as outlined above, or not. In the early days of AKD use, the claim of it being "cellulose-reactive" was never directly proven, but was deduced from the fact that it was impossible to extract all the AKD added to the paper using a non-hydrolysing solvent (such as chloroform) and that the paper, after solvent extraction, was still well-sized. Furthermore, the sizing was destroyed when the paper was firstly hydrolysed with alkali and then solvent extracted. The deduction about AKD's cellulose reactivity was thus not unreasonable, but it does not tie in with other evidence about the very slow kinetics of the reaction between more reactive diketenes (such as diketene itself) with water or with simple alcohols. Any reaction of AKD with such substances and even more so with cellulose would be expected to be sterically constrained to some degree by the presence of the alkyl groups. Because of this uncertainty, the unextractable AKD is often referred to simply as "bound AKD" rather than "reacted AKD" and this terminology will be used herein.

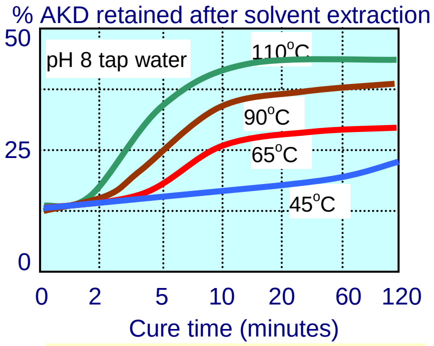
Much research was conducted into this area in the 1980s and this continues, albeit at reduced intensity, through to today. Perhaps the most thorough investigation was by Lindstrom and co-workers, from which several examples will be quoted to illustrate some basic effects of AKD sizing. All of this work (unless otherwise stated) is based on a simple AKD emulsified solely with cationic starch. Although the non-bound, intact AKD does contribute to sizing, its contribution is 30-50% (on an equal mass basis) of that from the bound AKD, but only when bound AKD is present. Non-bound, intact AKD on its own and hydrolysed AKD (the ketone) have no sizing effect.

The sizing level is therefore largely determined by the bound AKD, as shown in the figure at right for three different pulps formed into 80 g/m^2 handsheets. The interesting feature of this picture is the low quantities of bound AKD required for effective sizing, particularly of the commonly sized chemical pulps (eg 0.15 mg AKD/g bleached softwood Kraft pulp at 25°SR). These levels of bound AKD compare with typical addition rates of 0.5-1.5 mg AKD/g, which correspond very roughly to doses of the liquid emulsion of 1-4%. There was a good correlation between the AKD required to achieve a particular sizing level and the pulp's dry (not wet) specific surface area. Similar effects are observed with fillers of different surface areas as shown in this example for natural carbonates and here for PCCs.



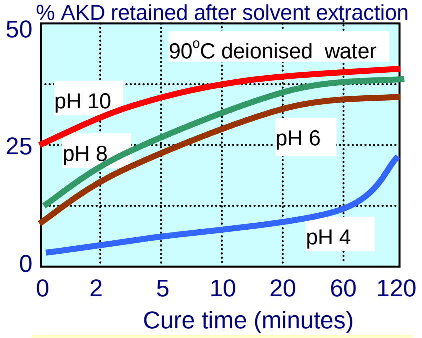
Source: Lindstrom et al in Nordic Pulp Paper Res.J., 1986, 1, 26-33.

One clear fact about AKD's dry end chemistry is its dependence on the temperature profile within the drying section, as shown in the figure at left for 80 g/m^2 handsheets that had been air-dried at ambient temperature for 5 hours before the stated curing time at elevated temperature. It is clear from this figure that the interaction between AKD and cellulose (in this case a fines-free bleached softwood Kraft) is slow at ambient temperatures, but that, even at high temperatures around 100°C, the timescale for complete interaction is longer than that available during drying on a paper machine. Extended drying (up to 20 hours) did not increase the proportion of bound AKD above 50% of that present in the paper.



Source: Lindstrom et al in Nordic Pulp Paper Res.J., 1986, 1, 34-42.

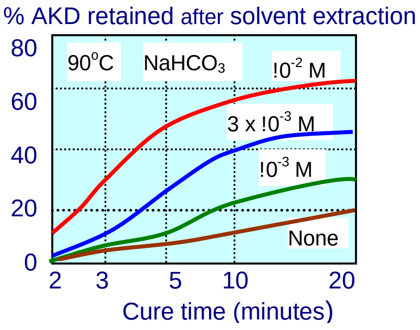
Other work has shown that AKD-treated papers dried under ambient conditions do ultimately become sized, but that this can take several days and also that AKD can migrate within the paper at such temperatures, ie high temperatures are not essential either for AKD re-distribution or its conversion to a sizing entity. This work also shows that the interaction between the AKD and cellulose does not begin until the paper is virtually dry, which is one of the further reasons why the detailed drying profile of the paper machine is so critical to the sizing achieved, particularly for machines using surface application.



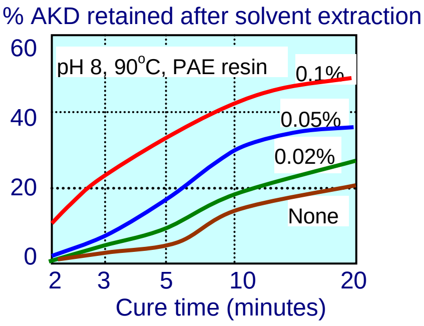
Source: Lindstrom et al in Nordic Pulp Paper Res.J., 1986, 1, 34-42.

As mentioned above, increased wet end pH expedites the sizing rate (see figure at right using same pulp as in above example, but where the sheets were not air-dried prior to curing at the elevated temperature). In this example, the pH was increased with sodium hydroxide, but sodium carbonate or bicarbonate are commonly used when this technique is applied on-machine to improve the sizing rate. (Partial dissolution of calcium carbonate filler also releases bicarbonate ions.) The addition of these chemicals does not change the wet end pH markedly due to the buffering effect of the equilibrium reactions involving bicarbonate/carbonate, but the pH in the drying sheet is higher than this due to breakdown of any free bicarbonate ion at elevated temperature plus the concentrating effect as water is removed during drying.

The effect of added sodium bicarbonate itself is shown in the figure at left below, which confirms its ability to act as an AKD cure promoter. PAE resins have been used with AKD sizes since their inception, partly as retention aids and partly as cure promoters. Laboratory tests have confirmed their ability to lift AKD retention, but this is quite small compared to their effect on the rate of cure of the retained AKD (as shown in the figure at right below). It is particularly important to note that, like the high dose of sodium bicarbonate, the high dose of PAE resin improves the AKD cure at low cure times. The mechanism for this effect is attributed to the base properties of the amine groups within the PAE resin, ie similar to that of hydroxyl groups. Elevated pH through the addition of either a strong alkali or sodium bicarbonate reinforce the cure enhancement from PAE resins.



Source: Lindstrom et al in Nordic Pulp Paper Res.J., 1986, 1, 39-45.



Source: Lindstrom et al in Nordic Pulp Paper Res.J., 1986, 1, 39-45.

These explanations for the efficacy of alkaline materials in promoting sizing with AKD are based on the premise that it does react with cellulose to form the β-keto-ester, which had not been proven at the time that the above work was done. Direct evidence for the formation of the ester had been sought for many years and was thought to have been finally demonstrated by Hercules in the early 1990s using solid state carbon-13 NMR. Partly because of the continuing uncertainty about whether this reaction is possible under papermaking conditions, further NMR studies have since been conducted in Japan as part of a large programme of work on AKD sizing over the last 10 years or so.

The conclusion from this work is that there is no evidence for β-keto-ester formation from NMR analysis of AKD-sized papers by direct comparison with a genuine cellulose β-keto-ester (prepared under non-aqueous conditions). This is further supported by the fact that a simple aqueous soaking of an AKD-sized paper in the presence of a nonionic surfactant destroyed its sizing and removed virtually all the AKD species, whereas this treatment had no effect on the prepared cellulose β-keto-ester. This suggests a possible mechanism for AKD sizing that does not involve ester formation:

- retention of AKD in the form of the intact lactone ring structure
- uniform distribution of the intact lactone during drying through melting
- orientation of the intact lactone with the alkyl groups facing outwards
- possible final hydrolysis to the more hydrophobic ketone.

This hypothesis still leaves open the answer to the question as to why, if there is no AKD reaction with cellulose, all the AKD species cannot be removed from a cured paper by solvent extraction (in contrast to the relative ease of removal by aqueous soaking). These two observations are rather difficult to reconcile so clear proof of the AKD sizing mechanism is still awaited.

Another important aspect of the AKD sizing process is the re-distribution of emulsified AKD droplets to form a uniform layer covering the surface of the particulate matrix. It had been assumed that this occurred by a classical spreading mechanism as the interfacial energy of AKD is well below that of cellulose and fillers. However, various studies have shown that AKD has a positive contact angle with cellulose (moist or dry), that allows only partial wetting. Similar conclusions have been reached by the use of atomic force microscopy to observe the spreading of AKD at different temperatures.

The form of the AKD is also relevant to spreading as the melting point of the ketone is substantially higher than that of the intact lactone, values of 79°C and 53°C respectively having been quoted for one commercial AKD. One reason why hydrolysis of AKD to the ketone at the wet end or during drying is thus undesirable is that spreading becomes more difficult due to the reduced time during which the sheet temperature exceeds the melting point of the AKD species present. An alternative re-distribution mechanism for the AKD is re-deposition by vapour-phase transfer, which again would be more difficult for any pre-formed ketone. Whatever the re-distribution or actual sizing mechanism, there is agreement that the surface coverage required for effective AKD sizing is quite low (well below 50%), but the normal measurement technique does not quantify the effective area covered by the splayed alkyl chains, only that covered by the central hydrophilic unit.

The issue of the final form of the AKD sizing entity is also relevant to three other important properties of AKD sized papers:

- the non-sizing characteristics of AKD-sized paper surface in terms of the paper's frictional properties (slip)

  Various studies have shown that AKD-sized papers have a lower coefficient of friction than papers sized with other chemicals. This has been attributed to both the bound and unbound components of AKD. The use of the alkenyl version of AKD overcomes some of these problems.

- the characteristics of AKD-sized paper surfaces in terms of lack of adhesion during production/use

  This problem has arisen in three different areas:

  - the manufacture of MG papers where AKD-sized papers do not adhere to the drying cylinder and thus give poor glaze in the product.
  - the conversion of plasterboard into the final product where AKD sizing gives poor adhesion of the plaster middle layer

- printing by laser or inkjet processes where AKD-sized papers give poor toner adhesion.

In the first two cases, alternative sizes have to be used (usually rosin and ASA respectively), but in the third case, AKD may still be used as the wet end size, but further sizing has to be carried out at the size press (see this example of the effect of starch and surface size addition on an AKD-sized base paper).

- ❑ the stability of the sizing over time.

As described above, the level of on-machine sizing achieved with AKD is dependent on various attributes of the sheet as it is dried. If the paper is surface-treated with starch, this will also affect the measured sizing level. The retained heat in the paper reel allows the sizing "reaction" to continue in storage, but sometimes the level of sizing is lost over time once the paper leaves the mill (see here for pictorial representation). This is referred to as size reversion or fugitive sizing and has been a particular problem with some AKD-sized papers, notably those containing PCC filler (see this example). This effect is discussed further under size reversion.

Alum

This is shorthand for aluminium sulphate.

Aluminium compounds

Aluminium is the second element in Group 13 of the Periodic Table. It is present in four sets of substances used in papermaking:

- ❑ aluminium salts such as alum, sodium aluminate, PAC, PASS and the nitrate, which can be used for:
  - sizing with rosin
  - overcoming pitch problems
  - for neutralising anionic trash
  - for improving adsorption/retention of anionic additives such as anionic dyes or anionic starch.
- ❑ chemically combined with silica as aluminosilicates in kaolin clays and bentonite clays, which are both quite chemically inert in papermaking systems
- ❑ various forms of alumina such as aluminium oxide itself, aluminium hydroxide and aluminium oxyhydroxide
- ❑ satin white pigment for speciality coating.

Aluminium hydroxide

This occurs in two possible forms in papermaking systems:

- ❑ as a precipitate that occurs when soluble aluminium compounds like alum are exposed to neutral pH conditions (see this diagram). As this precipitate can occur as a hard, adherent deposit, it represents a potential problem when soluble aluminium compounds are used for neutral sizing with rosin, particularly at high temperatures (>45^{o}C).
- ❑ as a speciality papermaking pigment in the form of precipitated aluminium hydroxide (or hydrated alumina) used for wet end and coating applications. It is supplied as a dry powder with a median particle size of 0.5-2 microns (depending on grade) and high brightness (> 95% ISO). As it is normally prepared from sodium aluminate, the pH of a dilute slurry is around 10. It can also provide flame-retardant properties.

Aluminium nitrate

This aluminium salt has been little used in papermaking to date, but has been tried at some German paper mills. The aluminium part of the chemical should function in a similar way to alum, except that the aluminium polymers formed in situ should be more cationic as nitrate is less likely to get involved in their formation. More importantly, however, nitrate can be used by many aerobic bacteria when the dissolved oxygen runs out, thus reducing the possibility for reduction of any sulphates that are present from other sources such as the fresh water.

Aluminium oxide (alumina)

This speciality pigment is used mainly for coating applications, where its highly-absorptive properties are particularly valuable for reducing ink setting and drying times in papers used for ink-jet printing. It can be used at the wet end, where its cationic character at neutral pH may be an advantage in systems from anionic trash (see this example of pH-charge effects).

Aluminium oxyhydroxide

This compound occurs as the natural mineral, boehmite, which is a crystalline form of AlOOH. It can be used for paper coating and has also been used as a retention aid. In the latter application, the boehmite is a cationic nano-particle with a diameter of 10-30 nanometres. It is supplied as a 35% colloidal solution and is reported to work particularly well in papermaking systems with high levels of conductivity and anionic trash.

Aluminium sulphate

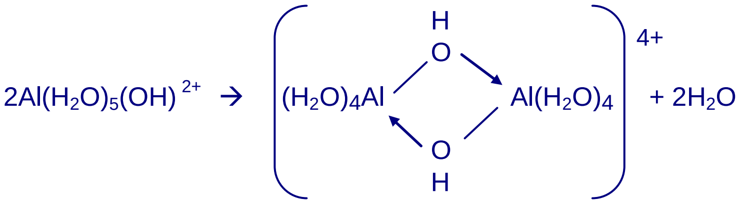
This is one of the two main water-soluble aluminium compounds used in papermaking and is often referred to simply as alum. The powdered form ($Al_2(SO_4)_3.16H_20$, molecular weight = 630 Daltons) is little used today as the liquid form is usually preferred on the grounds of ease of dosing and application. The traditional method of specifying the active content is as $Al_2O_{3,}$ but this is not that relevant to papermaking applications, where the Al content is more appropriate.

The aqueous chemistry of alum has been extensively studied in the context of alum's use as a coagulant in water treatment and as a paper sizing agent. As the reaction chemistry of alum is complex, even with only alum and water present, unexpected and/or undesirable reactions are always possible in real papermaking systems. One of the benefits of using pre-polymerised aluminium compounds (such as PAC) is that this uncertainty is reduced, albeit not completely eliminated as the aluminium polymers do still hydrolyse. The addition of alum introduces not only aluminium, but also sulphate ions, which can cause problems as a food source for troublesome sulphate-reducing bacteria. However, the presence of the sulphate anion seems to play a role in moderating the charge of aluminium complexes and may explain the observed superior sizing performance of alum versus aluminium chloride.

Alum’s reaction with water is a consequence of the aluminium ion’s high cationic charge and small ionic radius (0.06nm) leading to a series of possible reaction products, the nature of which depend on its concentration, the system’s pH and temperature and the contact time:

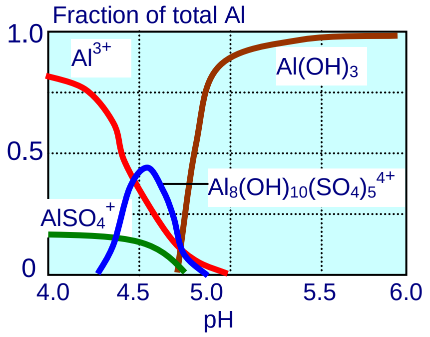
$$Al\,(H_2O)_6^{3+} \rightarrow Al\,(H_2O)_{6-n}\,(OH)_n^{(3-n)+} + nH^+$$

The octahedral complex with water molecules and the hydrolysis reaction both reduce the charge density of the aluminium species, thus making it more stable. Unless there is adequate buffer capacity present from dissolved alkalinity or calcium carbonate, this acidic reaction lowers the system pH. The picture is further complicated by the tendency of dissolved aluminium species to form polynuclear complexes through formation of hydroxyl (as shown at right) or oxygen bridges, processes called olation and oxolation respectively.



$$2Al(H_2O)_5(OH)^{2+} \rightarrow \left[(H_2O)_4Al \begin{matrix} H \\ O \\ \\ O \\ H \end{matrix} Al(H_2O)_4\right]^{4+} + 2H_2O$$

For solutions of non-complexing anions (eg chloride), the most commonly-accepted polymer formed at around pH 5 is $Al_8(OH)_{20}^{4+}$. The speciation of aluminium does depend on the anions present as some (eg sulphate) can themselves participate in the aluminium complexes, replacing some water molecules. A number of such complexes claim to have been detected and a simplified diagram for alum over the papermaking pH region is shown at right. In all such diagrams, the speciation curves tends to move to lower pHs as the concentration is raised. Insoluble aluminium hydroxide dominates the picture in the neutral pH band, but it carries a positive surface charge until pH 8-9, when the aluminate anion begins to predominate.

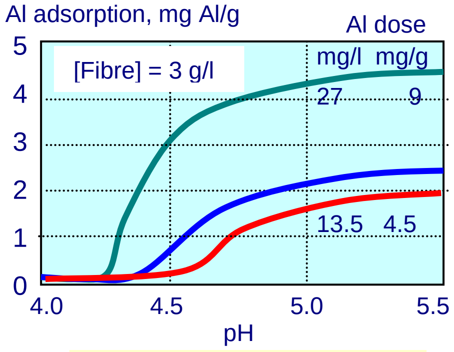


[Al] = 2.5 x 10-4 M = 13.5 mg Al/l

Reference: Tappi J., 1982, 65, 3, 125-130.

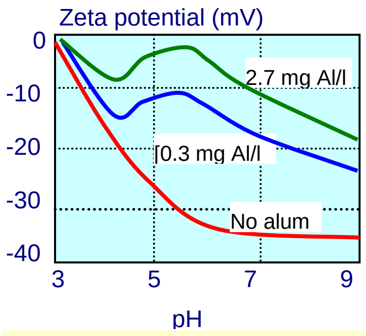
The optimum pH range for traditional rosin sizing (pH 4.5-5.5) coincides with the pH where the polynuclear complexes are formed and where the aluminium speciation changes rapidly with pH. This is one of the reasons why the wet end chemistry of systems containing alum is often rather unpredictable as the aluminium speciation is changing rapidly with pH and the kinetics of some reactions, particularly those involving the hydroxide, are rather slow. Another factor in the uncertainty associated with alum use is that, concurrent with providing a source of aluminium for coagulation, sizing or pitch control, alum is often (incorrectly) used for pH adjustment. As alum is not strongly acidic, this means that excessive quantities of alum are added, usually much greater than is needed to provide the amount of aluminium required. It is preferable to regulate pH independent of alum addition with either sulphuric acid or sodium aluminate, the latter also reducing the amount of alum required.

For alum to carry out its role in papermaking, it has to interact with another material and be retained in the paper. Frequently, the other material is the negatively-charged pulp surface. As shown in the figure at right, where alum was added to a bleached Kraft pulp, the adsorption of aluminium species starts to increase at about pH 4.5, which is coincident with the formation of polynuclear compounds and the level of dissolved aluminium continues to decline



Source: Arnson, 1983 Tappi Papermakers Conference, 37-44.

with precipitation of aluminium hydroxide. The adsorption mechanism is not only electrostatic attraction, as both the polynuclear compounds and the hydroxide can form hydrogen bonds with cellulose.



Source: Jaycock, Colloidal aspects of filler retention, 1st Intermatioal Seminar on Paper Chemistry, 1977.

The figure at left (from a different study) shows that very low concentrations of aluminium compounds can reduce the negative charge on the fibre surface as the cationic aluminium complexes are adsorbed. The hump in the charge-pH curves are again coincident with the formation of the most cationic aluminium compounds at around pH 5-5.5. Alum is able to improve particulate retention and drainage through these effects at acid pH. However, even with the relatively high alum doses used with rosin size, it would be normal to use another chemical, usually a single polymer, as the main retention/drainage aid.

The main reason why alum, even under acid conditions, is not relied on as the sole retention chemical is the relatively poor strength of the flocs produced compared to either a single polymer or alum combined with a polymer (see this example here). Although alum is not used primarily for retention/drainage improvement, there have been attempts to build retention aid systems around it. One of these was the Hydrosil system, which involved the use of alum with cationic starch under neutral conditions. This showed some early promise, but practical control problems appeared likely in view of the tight pH control needed to maintain the desired Al/OH ratio when the alum is added close to the flowbox.

It might have been expected that, with the trend away from traditional acid rosin sizing, the use of alum and aluminium compounds might have disappeared. This has not happened because techniques have been developed to use rosin (with its essential aluminium component) under neutral pH conditions and some oft-unrecognised side-effects of alum use have proved to be very valuable. These are its ability partially to suppress the dissolution of organics from pulps and to neutralise anionic trash. However, this interaction of aluminium species with pulp fibres has an adverse consequence, in that it leads to impaired fibre swelling with some pulps and hence reduced sheet strength.

Aluminosilicates

This mixture of oxides of aluminium and silicon has many different forms, but there are two broad categories used in papermaking:

- the natural aluminosilicate clays, notably the kaolin and bentonite clays
- the synthetic aluminosilicates formed when aluminium compounds are co-precipitated with silicas.

Amides

These are organic chemicals, more specifically organo-nitrogen compounds, containing the -CONH$_2$ group and can be looked on as acyl (RC=O) derivatives of ammonia. Amides are present in the very important category of polyacrylamides and the lesser-important one of glyoxalated polyacrylamides. The starting raw material for making chitosan (chitin) is an amide (acetylamine) derivative of cellulose.

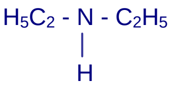
Amines

These are organic chemicals, more specifically organo-nitrogen compounds, containing the $-NH_2$ (amino) group. They can also be looked at as derivatives of ammonia in which one or more of the hydrogens has been replaced with an alkyl group. The terminology for amine chemistry is as follows:

- primary amines where the nitrogen atom is bonded to one carbon atom (see methylamine below)
- secondary amines where the nitrogen atom is bonded to two carbon atoms (as in diethylamine)
- tertiary amines are where the nitrogen atom is bonded to three carbon atoms (as in triethylamine).
- quaternary ammonium compounds are where the positive nitrogen ion is bonded to four carbon atoms (as in the tetra-alkyl ammonium chloride).

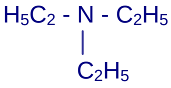
$H_3C - NH_2$

methylamine



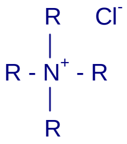
$H_5C_2 - \underset{\underset{H}{|}}{N} - C_2H_5$

diethylamine



$H_5C_2 - \underset{\underset{C_2H_5}{|}}{N} - C_2H_5$

triethylamine



$R - \overset{\overset{R}{|}}{\underset{\underset{R}{|}}{N^+}} - R \quad Cl^-$

tetra-alkyl ammonium chloride

All amines are basic to some degree (more so than ammonia itself) as they can be protonated under acid conditions to yield the corresponding ammonium salt, eg methyl ammonium chloride (CH_3NH_3Cl). The most useful functionality is the quaternary derivative due to its ability to retain its cationic charge at any pH (see this example for cationic starch). Because of this cationic property, amines are used to introduce amine functionalities into many papermaking chemicals:

- diethylenetriamine (having primary and secondary amine groups) to make PAE resins
- triethylamine to make AKD sizes
- alkylamines to make polyamines
- diallyldimethylammonium chloride to make polydadmacs
- chloro-hydroxy-propyl-trimethyl-ammonium chloride to cationise starches
- ethyleneimine to make polyethyleneimine
- melamine to make MF resins
- N, N, N- trimethylaminoethyl methacrylate to make cationic polyacrylamides
- alkylated quaternary ammonium compounds which are used directly as biocides and softeners.

Amino acids

These are organic chemicals containing two functional groups (amine and carboxyl), whose formula can be written as $NH_2 - X - COOH$. The simplest amino acid is glycine, $NH_2 - CH_2 - COOH$, which can also exist as $NH_3^+ - CH_2 - COO^-$, an amphoteric zwitter ion. All amino acids have a characteristic pH (isoelectric point) where they are uncharged, which is about pH 6 for glycine. Amino acids are the basic monomer unit in all proteins.

Ammonia

This substance is a gas at ambient temperatures and gives a weakly alkaline solution when dissolved in water:

$$NH_3 + H_2O \rightarrow NH_4OH \rightarrow NH_4^+ + OH^-$$

The pK_B value for the ionisation of ammonium hydroxide is 4.7 (at 25^{o}C) so the pH is about 9.3 when it is half ionised.

Ammonia as a gas or solution is not commonly used in papermaking, but ammonia may be generated in the system through the hydrolysis of any urea present. Amines are derivatives of ammonia in which one or more of the hydrogens has been replaced with an alkyl group. There are several papermaking compounds used in the form of ammonium salts:

- ammonium bromide used as part of biocide systems
- ammonium persulphate used for thermo-chemical conversion of starches
- ammonium zirconyl carbonate used as an insolubiliser
- ammonium salts of organo-fluorine compounds used for conferring grease resistance on paper
- ammonium salts of some anionic dyes.

Ammonium bromide

This is a recent addition to the list of oxidising biocides. Like sodium bromide, ammonium bromide can be oxidised by sodium hypochlorite to ammonium hypobromite. The form of the hypobromite and ammonium ions then depends on pH, which determines the balance of ammonium/ammonia and hypobromite/hypobromous acid.

$$NH_4Br + NaOCl \rightarrow NaCl + NH_4OBr$$

$$NH_4 \leftrightarrow NH_3 + H^+$$

$$Br^- + OBr^- + 2H^+ \leftrightarrow HOBr + HBr \leftrightarrow Br_2 + H_2O$$

This product was developed in Israel, where it has been used very successfully for several years as on-machine biocide at an Israeli mill before being licensed for use in other countries (to Hercules). The process was originally developed for protecting starch solutions from microbial attack, but this was then extended to use for microbial control within mill water circuits. The actual chemical interactions between ammonium bromide and hypochlorite are complex as a range of active compounds such as bromamines and chloramines could be formed, but the preferred term is “bromine-activated chloramines”. One particular niche appears to be paper machines with an alkaline pH (8 or so) where even bromine compounds are beginning to lose their efficacy.

Ammonium persulphate

This powerful oxidising agent is used to break down the starch chain during on-site thermo-chemical conversion of starch products. Its formula is $(NH_4)_2S_2O_8$.

Amphipathic

This term is applied to chemicals like surfactants, sizes and talc that have both hydrophilic and hydrophobic characteristics.

Amphoteric

This term is used for chemicals that have both acidic and basic groups within the same molecule. There are not many amphoteric chemicals used in papermaking, two being:

- proteins, where the substance becomes anionic as the pH is raised from the isoelectric point and cationic as the pH is lowered:

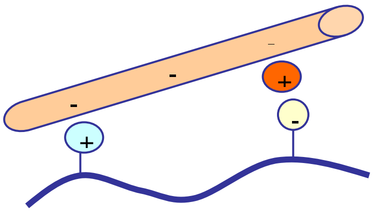
  $$^{-}OOC - R - NH_2 \xleftrightarrow{OH^-} HOOC - R - NH_2 \xleftrightarrow{H^+} HOOC - R - NH_3^+$$

- starches that contain both anionic and cationic groups within the same molecule. All cationic potato starches are amphoteric due to the native potato starch containing anionic phosphate groups.

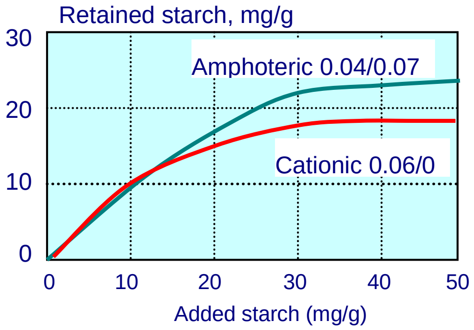
Amphoteric starch

Starches can be made anionic or cationic or be given both types of charge, which results in an amphoteric starch. As potato starches are naturally weakly anionic, cationisation produces what should strictly be called an amphoteric, rather than a cationic, starch. The anionic groups in the synthesised amphoteric starches are most commonly phosphate esters like the natural potato starches. In the discussion below, the amphoteric starches are those with synthetic anionic groups.

These starches have been used in papermaking for some time, but have been actively marketed for their claimed advantages by relatively few suppliers. This claimed benefit centres on their ability to be adsorbed (and hence retained) by either the electrostatic attraction between the cationic group and the anionic particle surface or by the agency of the tripartite interaction between the anionic surface, the anionic starch group and a cationic species such as calcium/aluminium ions or a cationic polymer (see visualisation at right).

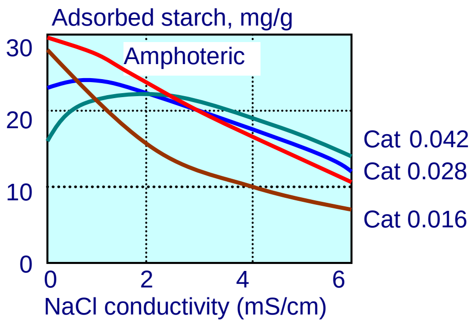


(Counter-ions not shown)



Source: Yoshizawa in J.Pulp Paper Science, 1998, 24, 7, 213-218.

There has been relatively little basic work on the adsorption characteristics of such starches and none of it substantiates any definitive superiority over cationic starches. One study using two starches prepared from the same native starch showed a better retention for the amphoteric starch on a refined bleached hardwood Kraft pulp (see graph at left, where the starch DS values are indicated as cationic/anionic), but the retention efficiencies were not high in the range where the performances diverged (ie above 20 mg/g dose).



Source: Malton in Appita J., 1998, 52, 4, 292-298.

A second study compared an uncharacterised amphoteric starch with three cationic starches (all from Tapioca) for their adsorption on an unbleached Eucalyptus pulp at pH 7 in the presence of varying concentrations of a sodium chloride. The graph at right shows a typical response to increased salt levels with the amphoteric starch showing the best adsorption below 2 mS/cm, but not as good as the higher cationic starches above this salt level.

Amylases

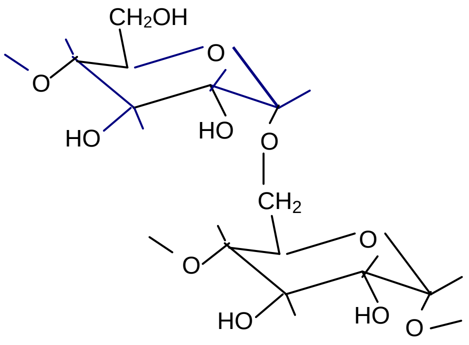
This is a generic name for a number of enzymes that catalyse the breakdown of starch molecules:

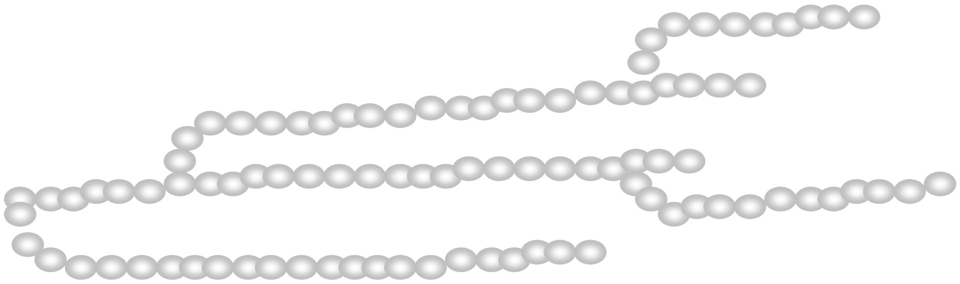
- α-amylase, which randomly hydrolyses the α 1,4- links in amylose and amylopectin
- β-amylase, which releases maltose units sequentially from the non-reducing end of the starch
- amylo-glucosidase, which sequentially hydrolyses the α 1,4- links in amylose and amylopectin starting from the non-reducing end to release glucose units

Of these, α-amylase is used at some mills in the on-site conversion of starches, mainly for size press application and all three enzymes could be used in various enzyme-based analytical methods for starches. The most recent application of such enzymes is for the cleaning of starch preparation/dosing equipment.

Amylopectin

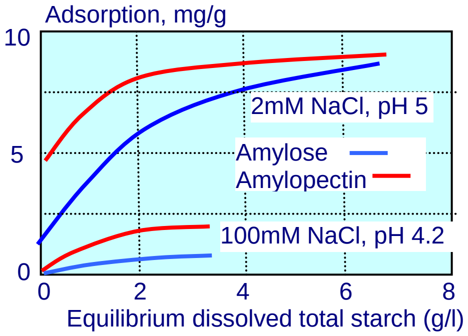
This is the major fraction of starch, accounting for at least 70% of its dry weight. It is a branched polymer with chains of α-1,4-linked glucose units connected through α-1,6 bonds at the branch points (as shown at right). About 5% of the glucose units are branched with each linear chain containing 20-30 α-1,4-linked glucose units (see representation below). For a molecule with 1-3M glucose units (200-500M Daltons molecular weight), its overall size is vast with a radius of gyration of 100-500 nm depending on the precise number of glucose units. Some starches (eg waxy maize) contain only amylopectin and no amylose. Because of its branched structure, amylopectin solutions have no tendency to retrograde.





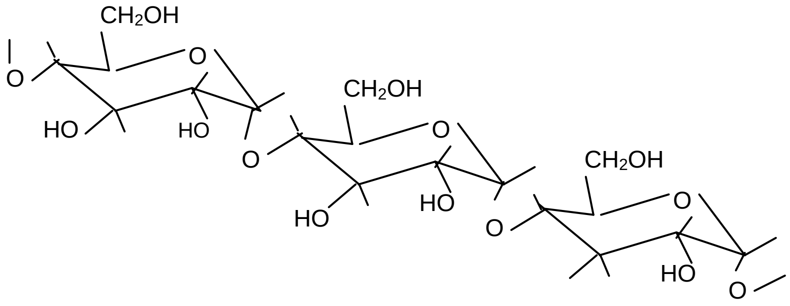
It would be expected, because of its much greater proportion and its higher molecular mass, that the amylopectin fraction would make the more significant contribution to the functionality of added starches. Consequently, it should be of value to know about the relative adsorption of these two components in the normal wet end guise of cationic starch.

This is illustrated at right in terms of the adsorption of a cationic potato starch (DS = 0.035) on a micro-crystalline cellulose with a total charge of about 10 μeq/g. The data shows adsorption at two different electrolyte levels (the pH levels also being slightly different due to ion exchange with surface protons). It is evident that both fractions are less well-adsorbed at high electrolyte levels, which is due to more shielding of the charge attraction between the cellulose and starch. However, the electrolyte level also makes a difference to the relative adsorption of the two starch fractions with preferential adsorption of amylose at the low electrolyte level and of amylopectin at the high electrolyte level. This effect is attributed to changes in the conformation of the two starch fractions because of their very different molecular sizes and structures. Another example is given here for the performance of amylopectin with colloidal silica.

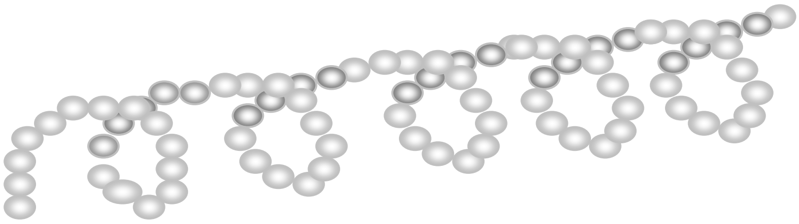


Source: van der Steeg, Nordic Pulp Paper Research .J.,1989, 2, 173-178.

Amylose



This is the minor fraction of starch accounting for no more than 30% of its dry weight. It is a linear polymer chain of α-1,4-linked glucose units with no branch points (as shown above). Some starches (eg waxy maize) contain no amylose, only amylopectin. Due to intra-molecular hydrogen bonding, the conformation of the amylose chain is a helix (see representation below), which can form inclusion complexes such as the well-known blue coloration with iodine. The amylose molecule is much smaller than amylopectin, containing a few hundred glucose units, but has a proportionately wider variation in chain length between starch types (see this table), eg the amylose in potato and tapioca starches has a much longer chain than in the cereal starches. Once dissolved, amylose has a tendency to precipitate because of intra-molecular hydrogen bonds - this process is called retrogradation and is responsible for the gradual opalescence of starch solutions on standing.



Anaerobic

In contrast to aerobic, this word simply means in the absence of oxygen and is particularly important in terms of the microbiology of the papermaking process. It is desirable to prevent or at least minimise the occurrence of anaerobic conditions as this leads to the most unwelcome types of microbial growth:

- ❑ the acid-producing bacteria that can convert simple carbohydrates like starch to organic acids and
- ❑ the sulphate-reducing bacteria that generate sulphides.

Even when dissolved oxygen is measurable in the bulk water of a papermaking stock, anaerobic conditions may be present beneath the surface of attached slimes close to the surface of pipes or tanks (see this picture of the various stages of slime growth). In these locations, anaerobic activity can have an accelerating effect on corrosion. Anaerobic conditions are deliberately created in anaerobic biological treatment systems, which are being used at a few mills to remove dissolved organics from process waters and thus minimise microbiological problems.

Analytical techniques

Monitoring the chemical status of the wet end is absolutely essential in order to understand the complex range of interactions taking place. In reality, many mills have inadequate data on machine chemistry other than occasional measurements of wire retention and pH. Surveys of wet end chemistry based on manual sampling and off-line analysis can be of undoubted value, but, as each sample only provides a "snapshot" of a mobile, dynamic system, the resources required to process the large number of samples is substantial. The major advance over the last 15 years or so has been the increasing availability and proven effectiveness of on-line monitoring systems for some parameters such as wire retention and charge. Nevertheless, the price of such systems is substantial and the benefits need careful appraisal in order to determine and then justify an economic payback.

Despite the above comments about spot sampling, any chemical data is valuable for solving problems when they occur as, otherwise, there is no information on the chemical status under "normal" conditions. The first task is to identify the optimum sampling locations and then to prioritise the parameters for measurement from those in the following table.

Parameter	Laboratory measurement technique
pH	Glass or antimony electrodes
Temperature	Thermometer or thermocouple
Electrolytes	Conductivity meter
Dissolved calcium	Ion chromatography, Ca electrode or EDTA titration
Dissolved organics	COD, organic carbon
Dissolved starch	Iodine coloration, enzymatic method
Entrained gases	Compressibility method
Cationic demand	Colloid titration or polymer titration with SCD end-point
Particulate zeta potential	Electrophoresis, streaming potential
Total consistency	Filtration and drying
Particulate ash	High temperature ignition
Fines	DDJ washing
Turbidity	Light scattering after filtration/centrifugation
Microbial content	Colony counts, ATP assay, slime coupons

Angstrom

This is a unit of length, normally used to measure atomic distances and bond lengths. It is equal to 10^{-10} m or 0.1nm.

Anhydroglucose

Literally, this word means glucose without water ($C_6H_{10}O_5$) and is applied to the glucose repeating unit in both starch and cellulose molecules.

Anions

This is the term for any simple ion that possesses a negative charge, the most common in papermaking being chloride (Cl^-), sulphate (SO_4^{2-}) and bicarbonate (HCO_3^-). It can also be applied to polymers with negatively-charge groups, but this is not common.

Anionic

This is the term to describe a substance that has a negative charge. In papermaking, this covers simple anions and more complex anionic polymers. It should be emphasised that all such polymers are actually neutral as supplied, but the term "anionic" means that the polymer backbone contains a number of anionic groups, which is often due to the presence of a carboxyl group. However, this anionic charge is always balanced by an identical cationic charge in the form of simple cations, such as sodium ions.

Anionic demand

This is a type of charge demand in which cationic substances in the sample react with added anionic chemicals. The anionic demand is measured by titrating the sample against a standard cationic chemical, usually a cationic polymer. The actual measurement technique is discussed further under colloid titration. Measurement of the anionic demand is not very common in papermaking as, in most cases, it is very low or zero. However, it is possible to measure both cationic and anionic demands in the one sample due to non-stoichiometric character of charge interactions. An example of where the anionic demand may be worth measuring is papermaking systems with a high addition of cationic additives, such as a machine making towel products, where the soluble anionic demand will give a measure of any non-adsorbed wet strength resin.

Anionic dyes

The charge on that part of the dye molecule that determines its colour properties is one way of classifying dyes. Anionic dyes include the traditional acid dyes and anionic direct dyes.

Anionic polymers

An anionic polymer is one with a number of negative charges on the polymer backbone, but with a balancing number of charges in the form of a simple cation such as H^+ or Na^+ associated with it. When dissolved in water, the repulsion between anionic groups on the chain gives the polymer an extended molecular conformation (see pictorial representation here).

Anionic polymers present in papermaking systems fall into two groups:

- ☐ those that have no particular functionality once in the papermaking system
  - the charged hemi-celluloses such as the glucuronoxylans in hardwood pulps and the arabinoglucuronoxylans in softwood pulps
  - lignosulphonates in pulps that have been produced with sulphite chemicals
  - the polyacrylates used as dispersants with filler or pigment slurries
- ☐ those that are added as functional additives
  - the anionic form of polyacrylamides used as retention aids at the wet end
  - the anionic form of starches (including the natural potato starches) added mainly to the paper surface in this form
  - carboxymethylcellulose (CMC) used as a strength additive, mainly for surface application.

In all the cases except the anionic retention aid, the anionic polymer gives the particles a negative charge, which contributes to their stability (resistance to aggregation). However, such polymers may also dissolve in the liquid phase, which reduces the particle's negative change and hence its colloidal stability. This might be considered desirable from the perspective of the particle's retention characteristics, but this is counter-balanced by several undesirable consequences:

- ❑ there is a loss of yield as the dissolved material is unlikely to be retained in the paper except on paper machines with very closed water systems
- ❑ the lowered particle charge reduces the swelling potential of the pulp fibres and their ability to adsorb cationic additives
- ❑ the dissolved substances become part of the undesirable anionic trash fraction.

On balance, it is preferable for such substances to remain with the wet end particulate matrix, as this allows the use of cationic additives that have good adsorption due to their charge attraction to the surface. However, keeping such substances with the pulp is not easy due to the ease of dissolution of what are inherent water-soluble substances. It appears that the majority of anionic substances in virgin pulps do not dissolve (eg less than 5% on refining a TCF Kraft pulp and 20-30% in bleached mechanical pulps), but this is not likely to be the case for previously-added polymers such as anionic polyacrylate dispersants.

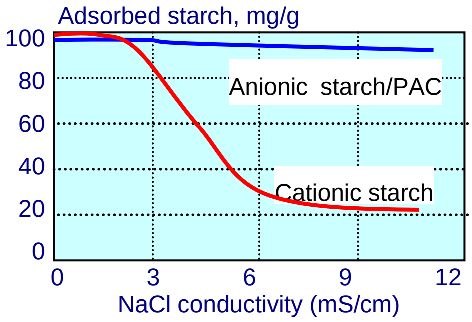
Even with an anionic surface charge due to the presence of polymers in the first category above, there are circumstances where the addition of wet end chemicals in an anionic form is preferable to the more normal cationic form. Examples are where there is a high level of dissolved multivalent cations (calcium or aluminium) present or where there is already a high addition of other cationic polymers. In these situations for example, an anionic polyacrylamide or anionic starch may be superior to a cationic polyacrylamide or starch.

Anionic starch

Potato starch is the only starch with a natural negative charge due to the presence of phosphate groups in place of some hydroxyls on the pendant $-CH_2OH$ group within the amylopectin fraction. The degree of substitution (DS) for these phosphate groups is about 0.004. As only one of the hydrogen atoms in the $-CH_2 - O - PO_3H_2$ group ionises over the pH range 6-8, the maximum anionic charge on potato starch in papermaking systems is about 0.025 meq/g. Starch esters in the form of phosphates (or acetates) can also be produced by the starch manufacturer and some starch ethers are also anionic, eg the carboxymethylstarches. In the thermo-chemical cooking of native starches, there is oxidation of some pendant $-CH_2OH$ groups to $-COOH$ groups by the oxidising agents present. Oxidised starches produced by the supplier also have some anionic character for the same reason.

Anionic starches are widely used at the wet end when alum is used for acid sizing with rosin, the cationic aluminium species helping to adsorb the starch onto the particulate matrix. Although this application declined with the move away from acid rosin sizing, it has shown some resurgence as a wet end starch in recent years through the difficulties encountered with cationic starch in certain papermaking systems. The use of purely anionic starches at the wet end does require the addition of a second component, either an aluminium compound or a cationic polymer, to fix the starch to the fibre.

In the example at right, the increased electrolyte level has a substantial adverse effect on the adsorption of a cationic starch (DS = 0.035) on a refined bleached hardwood Kraft pulp. However, the sodium chloride had very little impact on the anionic starch in the presence of PAC. Similar tests in the presence of dissolved calcium ions (up to 500 mg/l) showed a similar benefit in using the anionic starch/PAC combination.



Source: Brouwer at PTS Chemical Technology Conference, Munich, 1996.

In some papermaking systems, the use of anionic starch is constrained by the high activity of starch-degrading enzymes, but it is being successfully used for increasing dry strength of a diverse range of papers:

- ❑ fine papers filled or coated with gypsum, where the calcium sulphate leads to high dissolved calcium levels
- ❑ wet strength grades, where the anionic starch uses the cationic wet strength resin as the fixative, simultaneously helping resin retention and sometimes obviating the need for CMC
- ❑ coated wood-frees, where replacing the size press starch with 3% wet end starch allowed a 24% production increase in one trial.

Anionic trash

This term is applied to the range of negatively-charged substances (often polymers) that incidentally enter the papermaking system with other raw materials and then dissolve in the liquid phase. This set of substances is an important sub-set of problematic substances and are also sometimes referred to as interfering, disturbing or detrimental substances. If the anionic substances are not water-soluble or remain associated with the solid phase, they should not be classified as anionic trash. Indeed, the anionic substances remaining with the particulate solids are beneficial as they are responsible for attracting and adsorbing (cationic) additives onto the particulate surface. The factors which influence the dissolution of such substances from pulps is of obvious importance in understanding and controlling anionic trash.

The detrimental effect of this set of substances is that they are able to interact with added cationic additives due to the electrostatic attraction between the oppositely-charged groups (see this pictorial representation and these examples PEI and PAE resins). This leads to the formation of a 3-dimensional polymer complex/precipitate (a symplex), which has a lower charge than either interacting material and tends to be very hydrophilic and thus very water-retentive. This interaction is identical to that taking place in the important wet end measurement technique of colloid titration, which is the standard method to quantify the level of anionic trash (as the soluble cationic demand). Anionic trash substances released into solution from one particulate material (eg a pulp) are also able to re-adsorb onto other surfaces such as filler particles (see these examples for the effect of pulp-derived organics on filler charge).

The main sources of anionic trash are:

- ❑ negatively-charged hemi-celluloses present in virgin pulps, typically those containing glucuronoxylans
- ❑ lignosulphonates that are generated in sulphite pulping and present in virgin sulphite pulps and some chemimechanical pulps
- ❑ pectins present in virgin pulps
- ❑ saponified fatty acids that are naturally present in virgin pulps and also used as collectors in deinking
- ❑ sodium silicate used in deinking and peroxide bleaching
- ❑ polyacrylates dispersants used in filler slurries, notably for coating application
- ❑ oxidised starches used as size press additive
- ❑ volatile fatty acids that are generated microbiologically in papermaking
- ❑ sulphate present in fresh water and from alum addition
- ❑ humic acids in fresh water.

These problems can be controlled using the same hierarchy of techniques summarised generally for all problematic substances, which, in terms of anionic trash, are:

- ❑ selecting raw materials with the lowest possible content of anionic trash.

  Given the ubiquitous presence of anionic trash in virgin and recycled pulps, this approach is rather difficult in practice, particularly for virgin pulps. On the premise that the interfering substances present in recovered papers are principally derived from paper chemicals added in the previous cycle, papermakers producing grades that can be recovered and then recycled (ie most of them) should attempt not to use chemicals that will interfere the next time around. There should be some enlightened self-interest at work here as, unless avoiding action is taken, the original paper machine will experience some interference effects from its own broke.

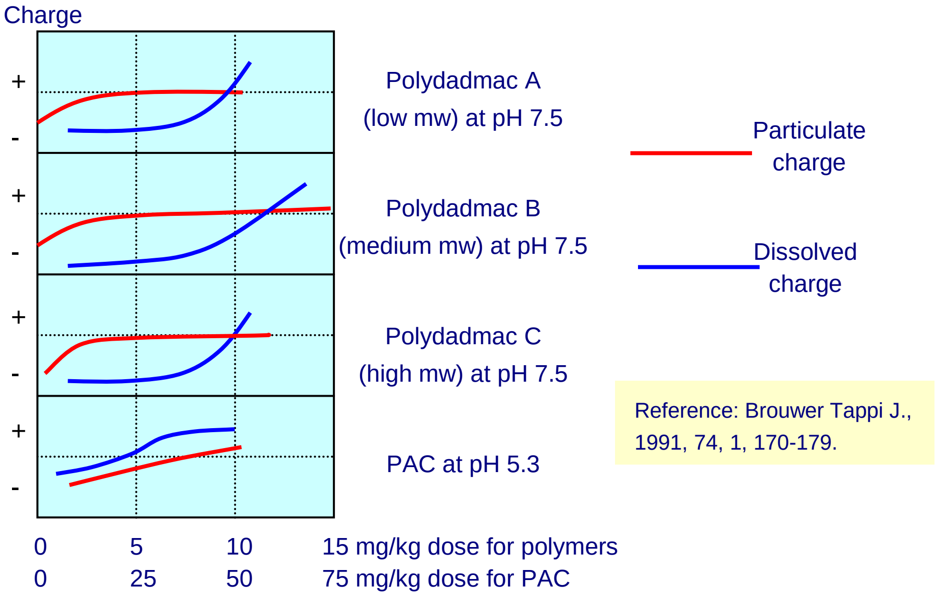
  The two notable sources of anionic trash in recovered paper/broke are size press starches (which also contributes significantly to another set of problematic substances - those available as a food source to micro-organisms) and coating dispersants. The use of cationic starches and cationic coating dispersants is one way to minimise these problems and give other benefits. For all pulps that are processed in some way before reaching the paper machine (all virgin pulps and deinked pulps), there should be adequate washing to remove as much anionic trash as possible.

- ❑ so far as it is practicable, optimising machine operation to minimise the opportunity for anionic trash to interfere with cationic additives.

  The first objective is to try to stop these substances dissolving at the wet end, which is not easy due to their inherent water solubility. Substances that do dissolve could be routed away from the machine system by thick stock dewatering (washing) and routing the filtrate away from the machine system for separate treatment. Biological treatment would not necessarily be the best treatment technique (as it is for the biodegradable substances responsible for micro-biological problems) for all anionic trash substances due to limited biodegradability of some (eg polyacrylates). Maximising the single pass retention of anionic trash is only possible through chemical treatment as discussed below. It may also be possible to move away from cationic chemicals to use either nonionic chemicals (eg PEO as a retention aid) or anionic chemicals (eg starch phosphate). The final option within this category is to optimise the cationicity of the additive (eg use more highly cationic starches).

- ❑ dosing of specific chemicals to neutralise the anionic trash with two slightly different approaches:

  - neutralise with cationic polymer, eg PAC, polydadmac, polyamine, PEI, super-cationic starch. This is the most common technique to deal with anionic trash and the key requirement is for the cationic polymer to interact with the anionic trash before any adsorption on the particle surface. The particle then remains anionic and still receptive towards any cationic additives to be dosed later. A good example of this is shown at right for a stock with about 15% filler content and moderate conductivity (1.7 mS/cm). The data demonstrates that, for this particular application, PAC is superior to polydadmacs (albeit at a lower, acid pH). Further tests showed that the retention of cationic starch (and fines) was much higher in the PAC-treated system (about 80% starch and 75% fines retention) compared to the best of the polydadmac systems (about 35% starch and 60% fines retention). However, despite this result for this particular pulp, polydadmacs are quite widely used for controlling anionic trash, one full-scale example for coated broke treatment being shown here.



Reference: Brouwer Tappi J., 1991, 74, 1, 170-179.

- treat with cationised adsorbent, eg talc, bentonite, zeolite.

A number of such products are available, but most results indicate their performance is no better than with cationic polymer alone.

Concentrations of anionic trash are usually measured by a charge titration of a sample filtrate or centrate with a cationic polymer and usually expressed as a cationic demand. The measured values on paper machines (usually in the form of meq/l) reflect not only the inputs described above and the degree of water closure, but also the effect of deliberate and incidental reactions with added cationic substances. Because of this, caution is required in converting measured concentrations to an input load. Some cationic demand levels are quoted here for several fluting/liner machines with fully-closed water systems.

Anisometric

This term refers to particulate materials that have unsymmetrical parts or unequal axes, eg fibres and clays.

Anisotropic

This term refers to substances or materials that have properties which depend on the direction of measurement. A good example is paper itself, which shows a definite direction-dependent strength due to the greater alignment of fibres in the machine direction.

Anomer

This is the name for the two isomers (α and β) of sugar molecules when they exist in a ring form (see glucose for further explanation).

Antifoam

Antifoam chemicals are able to prevent foam occurring in the first place and, together with defoamers and degassing chemicals, are an important component of most commercial foam control formulations. Anti-foams work by interfering with the foam-stabilising surfactants at a molecular level, examples being silicones and, where the surfactant is charged, organic polymers of opposite charge. Hydrocarbon oils are also effective as antifoams, but are little used in papermaking due to their tendency for deposition.

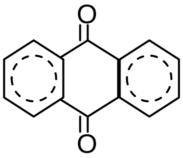
Anti-scalant

These chemicals are used in papermaking to prevent the formation of attached scales from precipitation of inorganic compounds. Their action is based on one of two principles:

- complexation of one of the participating ions, usually the cation, by the addition of chelants such as polyphosphates, which are commonly used in relation to calcium carbonate scales.
- crystal modifying agents such as certain phosphonates.

Anthraquinone (AQ)

This chemical (in the form of the most common isomer, 9,10-anthraquinone, formula at right) is sometimes used in chemical pulping processes (soda, Kraft and sulphite) to improve the process yield. It works by inhibiting the end-peeling reaction which removes monosaccharide units from the reducing end of carbohydrates. Some dyes are derivatives of anthraquinone, but these are little used in papermaking.

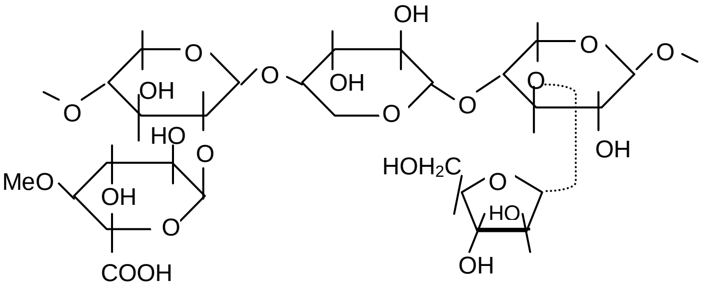


AOX

This abbreviation stands for adsorbable organohalogen compounds.

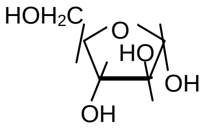
Arabinoglucuronoxylans

This is the main charged hemi-celluloses in softwoods, accounting for 5-10% of the wood. It is made up of a β-1,4-linked xylan chain with substitution by single side groups of arabinose and of α-1,2-linked 4-O-methyl-glucuronic acids on about 10% of the xylose units. Its degree of polymerisation is about 200.

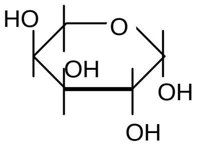


Arabinose

This is present at a low level in pectins and is one of the five simple sugars that are present in hemi-celluoses. It is a pentose with the formula $C_5H_{10}O_5$ and the structure shown here (drawn in both furanose and pyranose structures in the α-anomer form - see glucose for explanation of these terms).



Furanose form



Pyranose form

ASA

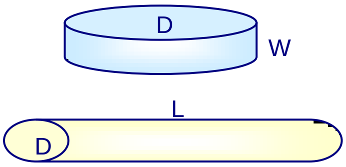
This is an abbreviation for the sizing agent, alkenyl succinic anhydride.

Ash

Measuring the ash content of paper products or of wet end samples is a common way to quantify their filler/pigment content. This is done by thermal combustion at a high enough temperature to burn off all the organic matter, but some fillers also lose some of their mass and this has to be corrected for in order to estimate the true filler content. There are two Tappi test methods available (at 525 and 900°C) depending on the predominant types of filler present. Kaolin clays lose their water of hydration (14% of their dry weight) over a wide temperature range and this is not complete until about 700°C. Calcium carbonates lose their carbon dioxide (44% of their dry weight) over a higher temperature range and this is not complete until about 900°C. Talc loses its water of hydration (5% of its dry weight) between 800-900°C. Titanium dioxide is stable up to at least 1000°C.

Aspect ratio

This term is used in relation to those papermaking materials with anisometric particle characteristics, notably fibres and fillers/pigments. For a disc-shaped particle (eg clay above at right), the aspect ratio is the diameter/width (D/W), whereas it is the length /diameter (L/D) for a tube-like fibre (below at right). This property is important in relation to the void volume (packing density) of particles, which is important for coating pigments.



Atom

An atom is the most fundamental unit of an element and comprises a compact nucleus of protons and neutrons with a number of electrons around it. The protons and neutrons are held together by the strong nuclear force, which prevents the nucleus flying apart due to the repulsion between the positively-charged protons. The neutrons are uncharged, but the mass of protons and neutrons is virtually identical, the best current measurement putting the value at 1.66053873 x 10^{-24} grams. The electron has a much smaller mass (about 1/1850th of the proton) and has a negative charge of exactly the same magnitude as the proton's positive one. As an atom is neutral, the number of protons and electrons is identical and this number (the atomic number, abbreviated as Z) determines the nature of the element and its position in the Periodic Table. The distribution of electrons around the nucleus is very important to the valency and hence chemical properties of the elements.

An element can exist in different forms depending on its number of neutrons and these different forms are known as isotopes of the element. For example, carbon has a principle isotope with 6 protons and 6 neutrons (labelled ^{12}C), but there are two other isotopes - ^{13}C with one extra neutron and ^{14}C with two extra neutrons. The atomic mass of an element is measured in atomic mass units or Daltons, which is 1/12th the mass of one atom of ^{12}C so one atomic mass unit or Dalton is the mass of one proton or neutron.

ATC

This is a sometimes-used abbreviation for anionic trash catchers, which are the (usually cationic) chemicals added to inactivate anionic trash.

Attractive forces

There are a number of basic forces that hold particles and dissolved substances together against the various repulsive forces that act in the opposite direction:

- ☐ electrostatic attraction between substances with unlike charges, which is a very important mechanism for the adsorption of water-soluble substances (normally cationic) onto the particulate matrix (normally negatively-charged) at the wet end. It also underlies the adverse interaction between cationic additives and anionic trash.
- ☐ hydrogen bonding between substances containing hydroxyl and amino groups
- ☐ hydrophobic associations (eg micelles) between molecules having some hydrophobic character
- ☐ van der Waals forces, which exist between all substances
- ☐ mechanical entanglement that occurs only between intact fibres and which can lead to fibre flocculation.

Auxochromes

These are functional groups that are incorporated in a dye molecule to deepen its colour and they also improve the dye's water solubility. These are mainly electron-donating (nucleophilic) groups such as hydroxyl and amino groups.

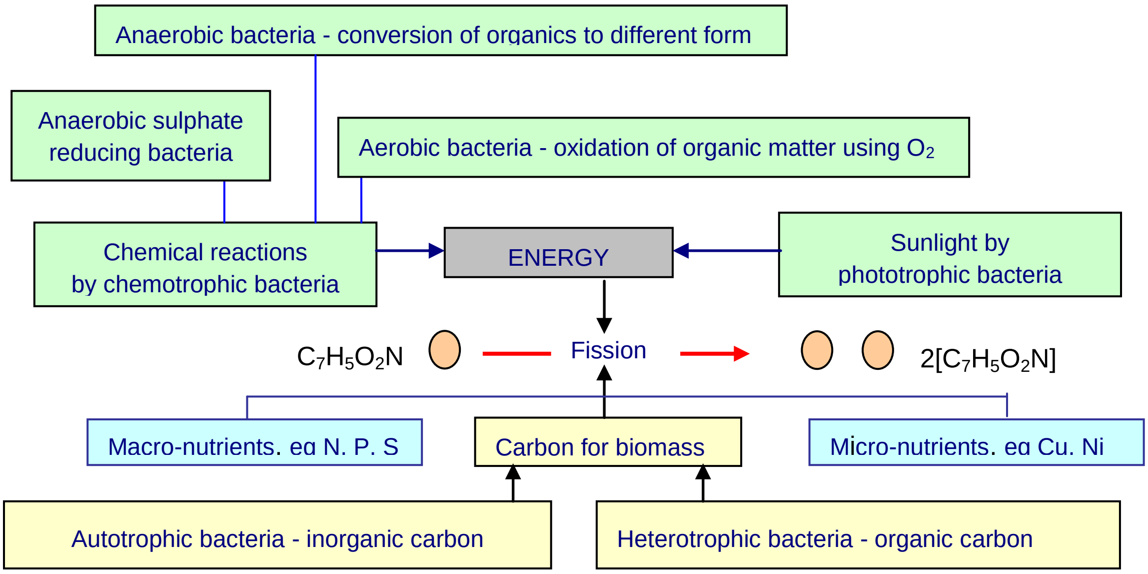
Azo compounds

These are organic compounds, more specifically organo-nitrogen compounds, that contain the group - N = N - . Such groups are present in many types of dye (see specific examples under acid dyes and direct dyes).

Bacteria

Being neither animals or plants, bacteria are single-celled micro-organisms belonging to the unicellular kingdom of the protists. They are responsible for most of the microbiological problems in papermaking, although there may be a contribution from fungi depending on process conditions. Bacteria represent very primitive life-forms and are classified on the basis of their cell morphology, their means of motility and their mode of reproduction. Bacteria are firstly allocated into different genera and then into species, eg *Bacillus subtilis* (usually written in italics) is one of many species in the genus Bacillus. A useful test used by microbiologists to differentiate bacteria into two classes is the gram stain, which involves the sequential addition of a crystal violet dye solution and an iodine solution followed by rinsing. Bacteria that retain the stain are called gram-positive and those that do not are called gram-negative, the staining characteristic being correlated with bacterial properties such as chemical resistance/susceptibility. In this simple way, it is also possible to distinguish between morphologically-similar bacteria.

Like all living things, bacteria need energy for maintaining themselves and a source of essential nutrients (carbon, nitrogen, phosphorous, etc) for growth of new biomass (see summary diagram below). The bacteria present in papermaking systems are all chemotrophic, in that they obtain their energy from some form of chemical reaction and are heterotrophic, in that their carbon comes form organic matter. The energy-producing reactions are usually oxidations and reductions involving organic compounds like dissolved starches (see microbiological chemistry). These reactions take place under either aerobic conditions, where dissolved oxygen is the final electron acceptor (oxidant) or under anaerobic conditions, where organic matter acts as both electron acceptor and donor. Bacteria are consequently classified as aerobes if they use O_2 or anaerobes if they cannot use O_2, Some bacteria are facultative in that they can operate under either aerobic or anaerobic conditions. Bacterial growth under anaerobic conditions is often called fermentation. A special type of anaerobic bacteria are the sulphate-reducing bacteria.

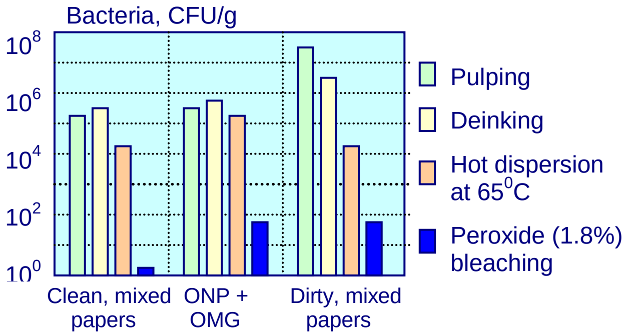


Bacteria in papermaking

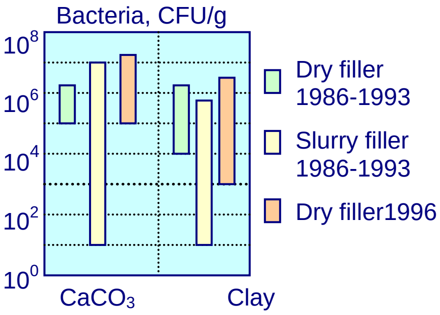
As bacteria are the most common cause of microbiological problems in papermaking, it is of obvious importance to know their possible sources and to endeavour to minimise their intake with all raw materials. All pulps contain bacteria, but recycled pulps tend to be more heavily contaminated than virgin pulps due to the opportunities for infection during use/collection and the presence of readily-available nutrients such as starch (see table at right for levels of aerobic bacteria in various pulps). Typical bacteria in recovered papers include *Bacillus* sp., *Micrococcus* sp., *Staphylococcus* sp., *Pseudomonas* sp., *Coryneform* sp., etc. Storage of all pulps increases the level of microbial contamination, particularly if left uncovered in the open.

Pulp type	Aerobic bacteria at 30°C (colony forming units/g)
Virgin pulps	up to 10^3
Clean wastepaper	10^2-10^3
Newsprint	10^3-10^4
Old corrugated cases	10^3-10^5
Mixed merchant paper	10^3-10^5
Mixed council waste	10^4-10^6
Raw mixed waste	10^6-10^{10}
Refuse-derived paper	10^5-10^9

Recycled pulps are subject to more pre-treatment stages than virgin pulps and, although none of these are aimed purposely at reducing their microbial content, this may be a useful side-benefit. The greatest potential reductions during pre-treatment are for deinked pulps due to the use of oxidising chemicals for bleaching. This is illustrated in the figure at right for three different grades of recovered paper. It is evident that flotation deinking has little impact on bacterial levels, but that hot dispersion (even at only 65°C) gives a useful 10 - 100x reduction. Bleaching in a final hydrogen peroxide stage is easily the most powerful treatment, although earlier addition of peroxide to the pulper had no effect on bacterial levels in this particular study. The biocidal action of peroxide is very dose-dependent with each 0.3% giving about a 100-fold reduction.



Source: Escabasse et al in Pulp Paper Canada, 1998, 99, 12, 106-109.



Source: Mentu et al at 1997 FRS Conferemce, Cambridge, England.

Another source of bacteria is the fresh water supply, but this is normally disinfected chemically prior to use. Control of the ingress of water-derived bacteria is most important at mills operating at a wet end pH close to that of the raw water, ie most neutral papermaking mills. Other raw materials almost certainly contain bacteria although the conditions during the manufacture of many chemicals will ensure their sterility, at least at the time of manufacture. As shown in the figure at left, a sustained sampling exercise over several years (mid-1980s to mid-1990s) in Finland has clearly shown that papermaking fillers contain substantial levels of bacteria. The greater variability of bacterial levels in slurry products is probably due to the presence or absence of biocides.

The microbial population at the wet end is a complex mixture of fungi (eg yeasts), aerobic bacteria and anaerobic bacteria. The balance between aerobes and anaerobes depends on process conditions, notably the dissolution of oxygen to make up for that utilised by the aerobes. Even in a well-aerated system with low concentrations of biodegradable materials, anaerobic conditions prevail in the quiescent zones close to pipe/tank surfaces. The microbial balance at the wet end depends on many other factors such as the degree of water closure and pH, acid conditions favouring the development of fungi as opposed to bacteria. The major slime-forming bacteria are common water-borne species such as *Aeromonas* sp., *Enterobacter* sp., *Klebsiella* sp. plus fungi such as *Phialophora* sp., etc.

Microbes are also present in surface application systems, particularly at the size press due to the preponderance of starches. Wet end microbes are unintentionally, but inevitably, retained in paper by the normal filtration mechanism and all microbes in surface-applied chemicals also end up in the paper. A major side-benefit of drying paper at high temperatures is the killing of most microbes due to the denaturation of proteinaceous cell components. The main exception is the spore-forming bacteria that possess heat-resistant surfaces. The microbiological quality of the final paper product depends on the input load and the temperature-time profile in the dryers.

An important element in the control of bacterial growth in papermaking is monitoring their background level in order to judge the effectiveness of the control technique being used. The traditional measurement technique is the standard colony count where a small sample is incubated under ideal growth conditions in the laboratory and the number of colony-forming units (CFU) counted after a certain time. This suffers from several disadvantages, notably the need for experienced microbiological expertise and equipment plus the time taken (2-3 days minimum) to get the results. Also, this technique gives the number only of those types of bacteria that grow under the particular conditions used in the test. Different conditions can be employed to give total aerobic bacteria, total anaerobic bacteria and important sub-types such as sulphate-reducers, but this requires even more equipment and can get very expensive. Most paper mills do not have the required expertise, so it is common practice to out-source this work, usually to the supplier of the control chemicals.

However, techniques, which overcome some of these limitations, have been developed for evaluating the overall level of microbes in the papermaking system:

- ❑ dip slides that contain the cultivation media and may be placed in the water to be tested. This gives an approximate level of bacteria by comparison to a reference without the need for specialist expertise/equipment, but still takes several days for completion.
- ❑ the use of dyes that respond to changes in the sample's redox potential, which becomes less oxidising as the growing bacteria use up dissolved oxygen. This is quite useful for the rapid evaluation (ca 1 hour) of different biocidal treatments.
- ❑ measurement of ATP (adenosine tri-phosphate), which is the energy-containing substance in all living cells. Once extracted from the cell, ATP is used by the firefly enzyme system luciferin-luciferase and this generates light in a bioluminescent reaction, which can be measured as an index of the bacterial concentration. There are several commercial instruments that utilise this technique to give results in minutes and it has been widely applied in papermaking by biocide suppliers.

These techniques are certainly an improvement in terms of the quick availability of results, but still do not provide information on specific problems such as the potential for slime growth. Fortunately, there are some simple ways to keep track of slime problems and also some newer techniques for on-line use and these are described further under that heading.

Bag papers

This is a sub-category of packaging papers and comprises a range of grades with two distinct categories in terms of surface finish - unglazed papers and glazed papers. The latter refers to papers made on a paper machine with a large, single drying cylinder, adhesion to which gives one side of the paper a glossy finish. Both types can be made from either unbleached Kraft or recovered paper for the brown grades and from bleached chemical or deinked pulps for the white grades. The papers are usually sized with rosin/alum as it is difficult to achieve the high glaze with synthetic sizes such as AKD and ASA. In fact, glazing aids based on rosin have to be used to obtain high glaze with AKD-sized papers in order to overcome the natural release characteristics of AKD.

Barrier coatings

This is a form of coating which is applied to papers or board to provide a barrier against ingress of water vapour, liquid water, grease, oil, gas, etc. The types of chemical used are:

- ☐ latices

  These are applied as a fine particle dispersion (typically 200nm diameter) using similar chemistries to those used for normal coating - styrene butadienes, acrylates, etc. The formulated coating may contain many other components (defoamers, biocide, chelant, thickener, and emulsifier) with typical addition rates of 4-15 g/m^2 (dry weight). Any normal coating equipment can be used, but rod or blade coaters are the most common. The aim is to achieve an even thickness rather than a flat surface and this is best done by a blade coater. It is desirable to use the highest possible dry solids content in the applied dispersion, but this is limited by the sudden, steep increase in viscosity above a volume fraction of about 50%. To act as an effective barrier, the latex dispersion has to be converted into a continuous film and this occurs as the latex particles coalesce when the water is removed during drying. The film formation temperature of the latex is critical and latices with glass transition temperatures of 10-40^{o}C are normal. Latex barrier coated papers are used in applications such as frozen food wrappings, food bags, etc.

- ☐ thermo-plastics

  These are mainly polyloefins such as polyethene (the most common by far) and polypropylene, but acrylate co-polymers are also used. They are applied by extrusion coating, which converts the solid thermoplastics into liquid molten state before application to the paper substrate. In order to improve adhesion between what are quite dissimilar types of surface, the hydrophobic plastic component is often pre-treated by a corona discharge. This generates ozone and free radicals, which oxidise the surface and make it more hydrophilic. Plastic-coated barrier papers are used in the most demanding applications such as milk cartons, juice cartons (with aluminium foil), other flexible food packagings and photographic papers (where the applied coating also contains minerals such as titanium dioxide).

- ☐ waxes

  These are applied at high temperature in a molten state usually by a roll applicator. These are usually paraffin waxes (ie pure hydrocarbons) and typically have a chain length of C_{18} - C_{20}. They are used in many commodity packaging grades such as corrugated cases and boxboards due to their low cost and ease of application.

In recent years, one of the criteria for such coatings has been its implications in terms of the paper's repulpability when recycled or other characteristics (eg compostability) when the used papers are dealt with in other ways.

Barium compounds

These are not common in papermaking, but there are two possible sources:

- barium salts, probably derived from virgin pulp due to the presence of barium in wood. The most likely ultimate form of any barium salts entering the papermaking system is insoluble barium sulphate as a wet end precipitate from the reaction with sulphate ions, which may come from the fresh water or alum addition
- from the deliberate use of barium sulphate as a pigment (called Blanc Fixe) in coating, most commonly in photographic papers, where it is used as a pre-coating because of its high chemical purity and inertness. Dispersions are often prepared using gelatin as a binder. Barium sulphate has a very high density (SG = 4.5) and a refractive index (1.66) somewhat greater than other common minerals.

Base

In contrast to an acid, a base is a substance that donates hydroxyl ions through its ionisation reaction:

$$BOH \rightarrow B^{+} + OH^{-}$$

where the equilibrium constant, $K_B = c_B.c_{OH}/c_{BOH}$ but $c_{OH} = K_w/c_H$

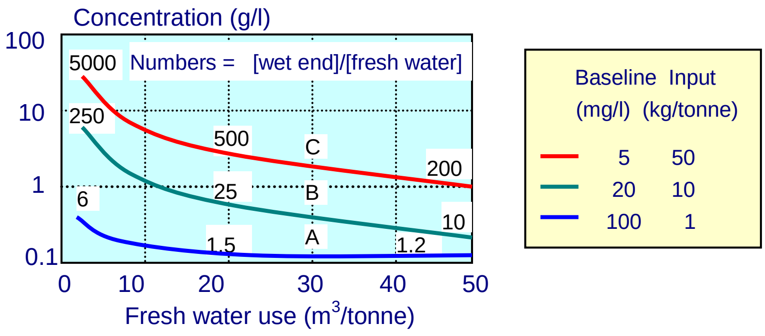
or $pK_B = pc_{OH} - \log(c_B/c_{BOH}) = pK_W - pH - \log(c_B/c_{BOH})$

where c is the concentration (moles/litre) of the subscript species

When the ionisation of the base is 50% complete (ie $c_B = c_{BOH}$), $pK_B = pK_W - pH$, so the lower the pK_B value, the stronger the base. The pK_B value for the ionisation of ammonium hydroxide ($B = NH_4$) is 4.7 (at 25°C) so the pH is about 9.3 when half ionised.

Baseline chemistry

This is defined in this document as the chemistry of the fresh water used on the paper machine and should be solely defined by the dissolved substances in the fresh water as any particulate materials should have been removed by prior treatment. Any substance present in the fresh water does not contribute to any build-up of that substance on closing up the paper machine's water system - it is only substances that originate from non-water sources that build up in this way. The build-up of dissolved solids on water closure can be modelled very simply as shown in the figure at right for three examples substances or sets of substances (note that the concentration axis has a logarithmic scale). The numbers above the lines are the ratios of the concentration in the machine system to that in the fresh water.



Line A could refer to dissolved calcium ions at a mill with a fairly hard fresh water supply. The input of dissolved calcium from other raw materials would be mainly due to dissolution of calcium carbonate, which occurs under acid conditions generated by pulps or by microbiological activity. As there is a relatively high baseline, the build-up ratio is relatively small at an input of 1 kg Ca/tonne, but the concentration still builds up to about 600 mg Ca/l at maximum water closure. In the case of a substance like calcium ions, this simple picture could be complicated by calcium ion exchange with either hydrogen or sodium ions associated with the negative charges on the particulate matrix and by the fact that calcium dissolution will probably itself vary with the degree of closure. Because of this, the wet end calcium concentration may build up on water closure more or less than predicted from a constant input load model and may even be less than the fresh water concentration.

Line B could represent the situation for total electrolytes, where there is a low level in the fresh water, but a substantial input and this is reflected in the higher build-up ratios. Electrolyte concentrations as high as this are usually only experienced at recycled liner/fluting mills (again due to calcium carbonate dissolution). Line C could refer to total dissolved organics, where the baseline level would be not far from zero at most mills. The assumed input level of 50 kg/tonne is the highest input level for any dissolved material and is again seen mainly at recycled liner/fluting mills, where it is largely starch-based. As a consequence of the very low baseline, high build-up ratios are inevitable.

The absolute value of the build-up ratio thus depends not just on the degree of water closure, but also on the input of that substance from non-water sources. All the calculations in the figure above assume that the input load of that substance is constant as the water system is closed up, but this may not be true, particularly for dissolved organics. In such cases, the actual build-up may not be as great as predicted in this simple model.

Basicity

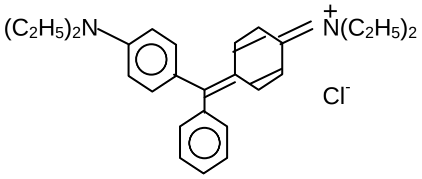
This is an alternative expression for alkalinity. The term is sometimes used in the chemistry of aluminium compounds to describe the character of polyaluminium chlorides.

Basic dyes

The traditional basic dyes now account for about 30% of overall dye use in papermaking. They have cationic trombones with balancing anions such as chloride or hydrochloride and are generally acidic to maintain the dye in a cationic form. Consequently, these dyes have good substantivity to pulps containing high levels of negatively-charged groups (mechanical and unbleached chemical pulps), but much poorer substantivity to bleached chemical pulps. Basic dyes are not as easily water-soluble as other dyes and dye solutions therefore often incorporate auxiliaries (acids and/or organic solvents such as alcohols) to keep the dye in solution. Because of this chemical complexity and potential adverse chemical interactions plus their poor light fastness, basic dyes are little used for surface application.

A common structure for many basic dyes is based on the triphenylmethane unit as shown at right for the dye, Brilliant Green. Malachite Green has a similar structure with methyl units simply replacing the ethyl units in the two amino groups. In this type of structure, the positive charge does not sit neatly on the quaternary nitrogen as shown, but is delocalised over nearly the whole molecule. Basic dyes are used mainly in the packaging sector for their strong colours and reasonable economy of use, despite their poor light-fastness.

Brilliant Green



Bauer-McNett classification

This is a widely-used technique to classify pulps into various particle size fractions. It uses a series of tanks separated by screens of steadily decreasing hole size through which the pulp suspension is passed. The most common mesh sizes and corresponding screen openings are shown in the table at right. The third column shows the average fibre length (from Kajaani Fibre Length Analyser) retained on that screen from a study using a TMP and Kraft pulp both from spruce. The average fibre length of the fines (defined as that passing a 200 mesh screen, abbreviated P200) was 0.12mm. The long fibre fraction is sometimes taken as the fraction retained on the 28 mesh screen (abbreviated R28).

Mesh size	Hole size (mm)	Fibre length (mm)
10	1.68	-
12	1.41	-
14	1.19	2.8
20	0.84	-
28	0.60	2.0
48	0.30	1.3
100	0.15	0.69
200	0.075	0.28

BCDMH

This is an abbreviation for the biocide, bromochlorodimethylhydantoin.

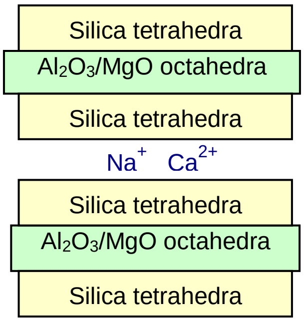
Beating

This is a term for the mechanical treatment of pulps that took place in "beaters". Whilst this type of equipment is still used by a few mills, it has largely been replaced by refiners.

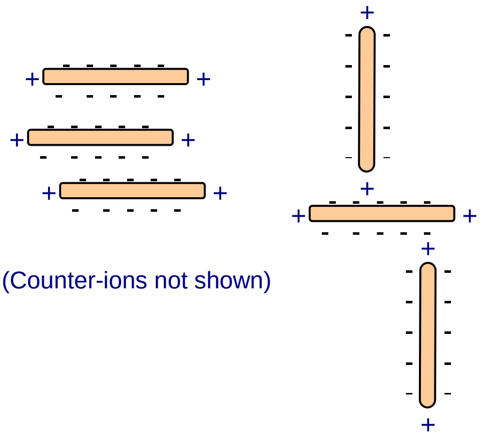
Bentonite

This is the generic name for a range of natural smectite clay minerals that are comprised predominantly of montmorillinite (named after one of its sources in France) with lesser impurities such as quartz. Its chemical form varies with local geology and only a small number of the natural deposits are suitable for papermaking, notably the white-coloured deposits with a low iron content.

The structure of montmorillinite bears some resemblance to that of talc (as shown in a simplified form at right), but it is more complex. Whereas talc has only magnesia octahedra in the central layer, montmorillinite also has some alumina, but there is an overall deficiency of cations which is made up by the more loosely-held sodium and calcium ions. The overall formula of montmorillinite is very variable, but it can be approximated as $(Na,Ca)(Al,Mg)_6(Si_4O_{10})_3(OH)_6.nH_2O$. Its often-brown colour is due to the presence of iron, which replaces some of the aluminium or magnesium ions. As the iron is associated with the crystalline structure, it cannot be removed chemically. Most natural bentonites contain montmorillinite in the predominantly calcium form, but they also exist naturally in the sodium form (eg the Wyoming bentonites from the USA).



Like all clays, montmorillinite has a platy or flaky structure. Its dimensions are about 300nm by 100nm for the face with each platelet/flake having a depth of only about 1nm when the material is fully delaminated. The structure of montmorillinite means that the flat silicate surfaces are negatively charged, whereas the alumina/magnesia edges are slightly positively charged. The charge arises from isomorphous replacement (eg of silicon by aluminium ions in the outer layers) and the presence of alumina (in place of magnesia) in the middle layer. Natural bentonites have a cation exchange capacity of 0.7-1 meq/g (ie much higher than that of kaolin clays). The weak forces between the clay platelets and the presence of hydrated cations allows the ingress of water and the swelling of the clays, but this is much greater when the loosely-held cation is the sodium rather than calcium form. Bentonite suspensions exhibit thixotropic characteristics as the platelets tend to orient edge-to-face ("house of cards" structure) under quiescent conditions, but shearing aligns the platelets and lowers the viscosity (see picture at left).



(Counter-ions not shown)

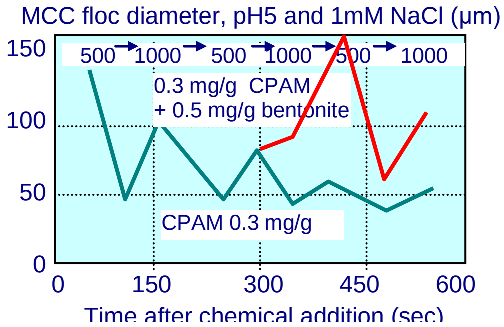
Bentonites are used in two forms in papermaking:

- the alkali-activated bentonites that are treated with soda ash to convert the bentonite to the fully sodium form, thereby removing the calcium as a carbonate precipitate. The swelling ability of these products corresponds to a water content of 20-40 ml/g with a very high potential surface area (about 800 m^2/g). This preliminary treatment of bentonite replaces the exchangeable calcium ions with sodium ions, but these can themselves be replaced when the bentonite is prepared in hard water or when the prepared suspension is added to the papermaking system, which invariably contains some calcium ions. This can lead to flocculation of the bentonite and loss of performance. Sodium bentonites are widely used as part of retention/drainage aid systems and have also found applications for pitch control (see here for example with a polydadmac).
- the acid-activated calcium bentonites are used in the back coating of carbonless-copy papers.

The largest application of bentonites are as retention/drainage aids, but this is always with an organic polymer as part of a dual component system as bentonite alone has no efficacy. There are two main retention/drainage systems based on bentonite - the Organosorb/Organopol system for newsprint mills and the Hydrocol system for fine and other paper mills, both using bentonite with a polyacrylamide and both developed originally by Allied Colloids (now Ciba). However, bentonite is also used successfully with other polymers such as polydadmacs and PEI.

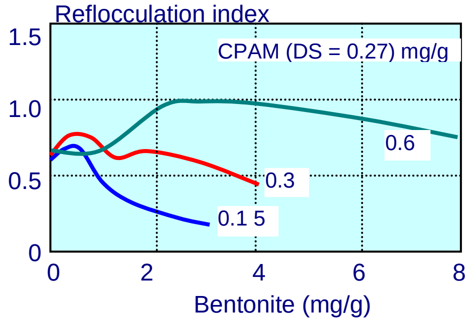
In the Organosorb system, the bentonite is added first to adsorb the organics that would otherwise interact adversely with the cationic polymer (Organopol) which is added later. In this way, the load of dissolved organics can be lowered by as much as 50%, giving a significant secondary benefit in terms of wastewater loads. Another positive attribute from the presence of bentonite is its tolerance of residual silicate in deinked pulps (see this example). The Hydrocol system purposely uses a high dose of cationic polyacrylamide (up to 2 kg/tonne paper) to the thick stock to give an over-flocculated system which is then sheared down on passage through the fan pump. The late addition of the bentonite (up to 4 kg/tonne) reforms the floc structure, but in the form of smaller micro-flocs that give not only good retention, but also improved drainage and good formation (see example here). Results for one mill changing from a single polymer retention aid to Hydrocol showed increased wire retentions for filler of 52 to 75% on a wood-free grade and 27 to 50% on a wood-containing grade.

Shown in the two figures below is data from some interesting work on the shear resistance and reflocculation ability of bentonite/polyacrylamide systems. In this work, the shear is cycled between two levels by varying the impeller speed in a DDJ (see comparative data for various polyacrylamides on their own here). In this experiment, the dose of polyacrylamide (DS = 0.27) corresponded to the charge of the cellulose surface (10 µeq/g). It is evident that, even though the bentonite is added quite late (by which time the conformation of the polyacrylamide chains would be quite close to the cellulose surface), it is still able to enhance flocculation. This is rather similar to the normal mode of bentonite addition with polyacrylamides.



Source: Swerin et al in J.Pulp Paper Science, 1997, 23, 8, 374-381.

The data from these experiments can be re-plotted in the form of a reflocculation index, which is the ratio of the floc size after and before the first high shear period at 1000 rpm. This is shown at right for the same cationic polyacrylamide as in the figure above, but at three different dose levels (0.15-0.6 mg/g). This confirms that bentonite enhances the reflocculation ability of cationic polyacrylamide, but the optimum bentonite dose moves to higher levels as the polymer dose increases. The optimum dose of bentonite is 3-4 times the corresponding optimum dose of colloidal silica (see here). Comparative data is also shown here for the same polyacrylamide in a dual treatment with polyethyleneimine.



Bicarbonate

This is a very common anion (HCO_3^-) in paper machine waters and may originate from several sources:

- associated with calcium or magnesium ions as temporary hardness salts in the fresh water
- from deliberate or incidental dissolution of calcium carbonate
- from addition of sodium bicarbonate or carbonate to boost the alkalinity, usually to help sizing with AKD.

When bicarbonate is present incidentally (in fresh water and from calcium carbonate dissolution), it can cause difficulties with some additives (eg with glyoxalated polyacrylamides) and because of its participation in various ionisation reactions:

$$CO_2\ (g) \overset{k_H}{\leftrightarrow} H_2CO_3 \overset{k_1}{\leftrightarrow} H^+ + HCO_3^- \overset{k_2}{\leftrightarrow} H^+ + CO_3^{2-}$$

As the values for pk_1 and pk_2 are 6.35 and 10.3 respectively at 25°C, bicarbonate is the dominant form within the pH range 7-9. This is little affected by changes in temperature over the range 10-50°C.

The potential problems arise at either end of the above reaction sequence:

- under alkaline conditions when it forms carbonate ions, which may precipitate calcium carbonate (perhaps in a different part of the same system in which calcium carbonate dissolved)
- under acidic conditions, when it releases carbon dioxide, which may cause entrained gas and foam problems.

There is another ionisation reaction that occurs at elevated temperatures as the paper is dried:

$$HCO_3^- \leftarrow\rightarrow CO_2 + OH^-$$

Any bicarbonate that exceeds the amount needed to precipitate the dissolved calcium present (as calcium carbonate) can participate in this reaction to release hydroxyl ions, which then elevates the sheet pH in the small amount of water present just before the sheet becomes dry. This is the way that added bicarbonate (or carbonate) ions help AKD sizing. Once the sheet has cooled down, atmospheric carbon dioxide re-buffers the sheet to a more neutral pH.

Binder

This term is usually reserved for the various types of polymer used to hold together the pigment particles in coating formulations. There are several types:

- natural water-soluble polymers, the main ones being starch, carboxymethyl cellulose and proteins
- synthetic water-soluble polymers, the only significant one being polyvinyl alcohol
- synthetic polymers not soluble in water (latices), the main ones being styrene-butadienes, styrene-acrylates and polyvinyl acetate.

Binders (or usually combinations of binders) are selected on the basis of their effect not only on the strength of the coating layer, but also on other characteristics such as porosity, optical properties, ink absorption and on the rheology of the coating mix. Water-soluble binders have a much greater impact on the viscosity of the coating mix than latices and they can be ranked PVOH, CMC, protein and starch in order of decreasing thickening ability. The quantity of binder in a coating depends on the binder demand, which reflects the solids content of the mix and the packing of the pigment. A short summary of their relative functional effects is given in the table below.

BINDER	At equal doses			At equal binding power		
	Cost	Binding power	Water resistance	Gloss	Ink absorption	OBA retention
SB latex	2	2=	1	1	5	5
Starch	1	5	5	5	4	4
Protein	3=	4	2	4	1	3
CMC	3=	2=	3=	2=	2=	2
PVOH	5	1	3=	2=	2=	1

Where 1 = highest/cheapest and 6 = lowest/most expensive

Source: Lanham "Coating binders" in "Introduction to Aqueous Pigment Coating", Pira Course, 1989.

Binders are important in relation to wet end chemistry due to their presence in coated broke and their consequent contribution, for water-soluble binders, to the level of dissolved organics at the wet end and, for insoluble binders like latex, to wet end deposition problems such as white pitch.

Biochemical oxygen demand

This is a measure of the oxygen consumed during incubation of the water sample, usually for a period of 5 days, in the presence of nutrients and bacteria. It is not often measured at the wet end of paper machines, but is an important measure of the losses of biodegradable compounds in the mill wastewater. Chemical oxygen demand (COD) is more commonly measured at the wet end as an index of total dissolved organics (ie both biodegradable and non- biodegradable substances).

Biocide

A biocide is a chemical able to kill some form of life, but, in papermaking, the term is used solely in relation to micro-organisms (sometimes therefore called a microbicide), which are bacteria (killed by bactericides) and fungi (killed by fungicides). The addition of biocides is the most common way to control microbiological problems at the wet end of the paper machine. Biocide addition for disinfection of water is covered here. An ideal biocide should fulfil four requirements:

- be effective at a low concentration with broad spectrum activity
- be compatible with other wet end materials
- be safe to use in terms of worker exposure during handling and
- residues should be degradable and have no effect on aquatic life in natural systems.

Biocide formulations often contain several active ingredients to provide a broad spectrum activity plus dispersants/surfactants/solvents to aid distribution and penetration of existing slimes. An important factor for many applications, notably in food contact papers/boards, is that the biocide should have been approved under local regulations such as the US FDA and/or the German BGVV systems. As these chemicals are amongst the most hazardous used at paper mills, their safety and wider environmental attributes have become more important in recent years.

On-machine biocides can be broke down into two main categories:

- oxidising biocides, which are similar to those that are widely used for water disinfection, the main ones used on the paper machine being:
    - chlorine and bromine release agents such as the bromochlorohydantoins
    - chlorine dioxide
    - ammonium bromide, which is used with sodium hypochlorite
    - hydrogen peroxide or peroxy compounds such as peracetic acid
    - ozone.
- organic biocides, which can be sub-divided according to the presence of key elements into:
    - organo-sulphur compounds
    - organo-halogen compounds
    - organo-nitrogen compounds
    - organo-phosphorous compounds
    - miscellaneous organic compounds such as gluteraldehyde.

Points of biocide application are numerous, but they are most commonly added to the thin stock and backwater systems for several short periods each day rather than continuously. Direct treatment of possible sources of infection such as cooked starch solutions is also important as microbial degradation could otherwise lead to a range of problems from impaired starch adsorption and consequent poor performance to pH depression (and its various consequences) from the acidified starch solution. Biocides are also used as preservatives in the product, but this requires addition to the paper surface as normal biocides are usually selected on the basis of not being retained in the paper.

Biodegradability

Biodegradable substances can be broken down to simpler substances by microbial action and there are various standard test procedures to assess a substance's biodegradability under various conditions. It is a property that is usually considered to be desirable on environmental grounds, but this may not always be the case as it depends on where this action takes place. A biodegradable material will be broken down to some degree during papermaking and this is likely to be greatest for biodegradable materials with a low single pass retention (ie dissolved substances such as starch), which are circulated many times around the papermaking system depending on the machine's degree of water closure. The substance's biodegradability is responsible for the costs of controlling microbial-related problems such as slime and it also impairs the material's functionality to some degree. This set of on-machine problems that stem from a material's biodegradability turns to an advantage in terms of the non-retained residues in the mill wastewater as these can then be easily removed by biological treatment. If the mill does not have a biological treatment plant, biodegradability of wastewater components leads to oxygen consumption in the receiving water, which may or may not lead to problems depending on the water's oxygen balance.

Biodegradable materials in the paper product lead to possible biodeterioration of the paper when stored under moist conditions. After use, some biodegradation is inevitable in the waste stream, even before the product might be recovered for material recycling. Landfill of wastepaper eventually leads to the breakdown of biodegradable components provided conditions (eg moisture) are suitable. In this situation, biodegradability is useful if the methane gas thus produced is utilised for energy production, but is harmful if the methane is simply released to atmosphere due to its high global warming potential. Lack of biodegradability (or of abiotic degradability) denotes that the material will tend to persist in the environment once it is released. In the aquatic environment, such substances may build up to levels which exert direct toxic effects on aquatic life, perhaps after bioconcentration in fatty tissue, depending on the substance's chemistry.

As there are no paper chemicals with guaranteed 100% overall retention in the paper and as there is always the risk (however slight) of spillages, biodegradability is, on balance, a desirable attribute for all organic papermaking materials. This is not yet the case, although it is one of the motivations behind the development of new paper chemicals. However, when a papermaking raw material is biodegradable, it is of paramount importance that it is retained rapidly in the paper, ie it should have a high first pass retention not just a high single pass retention in order to minimise degradation of its functionality.

Biofilm inhibition

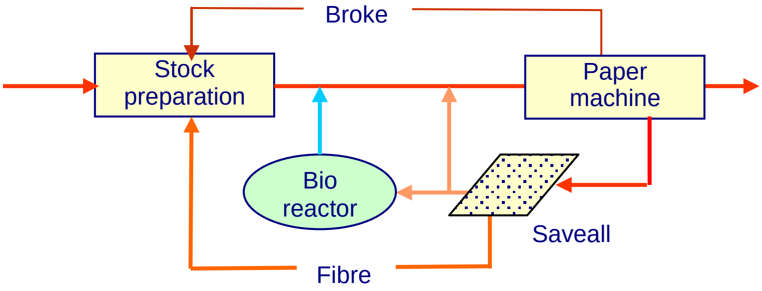
This is one of the newer techniques to stop the formation of slime on machine surfaces, which is one of several problems resulting from inadequate microbial control. Most of these techniques are based on chemical treatments that interfere with the processes of microbial attachment and adhesion, some examples of commercial techniques being:

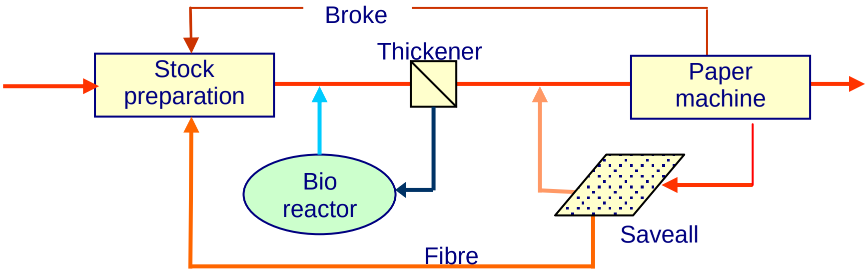
- mixtures of paraffins and terpenoids
- mixtures of surfactants and lignins, an additional benefit of which appears to be the ability to reduce the number of bacteria in a spore state, ie the type of bacteria that are able to survive the high temperatures in the drying section and which contribute the majority of the microbes in the dried paper at the final reel.
- electrochemical treatment that alters the chemistry of the actual surface.

Biological treatment

This term is most commonly used in the context of treatment of combined machine wastewaters outside the mill, but such systems can also be integrated closely with the paper machine system. In this way, they have the potential to remove biodegradable organics from machine waters and thus make a significant contribution to minimising on-machine microbiological problems. Biological treatment harnesses a community of bacteria and sometimes higher life-forms to remove biodegradable organics like starch. The processes are operated either aerobically, where the products of biodegradation are carbon dioxide, water and more biomass or anaerobically, where the products of biodegradation are carbon dioxide, methane and more biomass (but much less than in an aerobic system). This overall concept is not widely utilised at present, the few full-scale examples being at 100% recycled mills with fully or substantially closed water systems. As shown in the two examples below, the water for treatment can be sourced from at least two locations.

The first example below at right simply removes water from the machine's backwater system and passes this to the bio-treatment plant with the treated water being returned to the same system, albeit downstream from the off-take point. Both aerobic and anaerobic treatment processes have been used in this way, but the most prominent full-scale examples (at European recycled fluting/liner mills) are based on an initial anaerobic stage, where most (80-90%) of the organics are removed, followed by a small aerobic stage. As well as removing carbonaceous BOD, the anaerobic stage is able to remove much of the sulphate through its reduction to sulphide and subsequent removal with the off-gas and the aerobic stage is able to remove much of the dissolved calcium by precipitation as calcium carbonate. These latter processes are very beneficial in terms of the recycling of the treated wastewater to the papermaking system.





In this second (much less commonly-applied) case, the dissolved solids from the input pulp and broke are removed by washing or thickening the combined thick stock, passing the filtrate to the bio-treatment stage and the cleaned pulp to the paper machine. This should be superior to the above application as the substances are removed before the thin stock system and this further limits their build-up in the primary and secondary loops. Where broke is the dominant source of dissolved organics, this treatment could be applied to just the returned broke line in order to minimise costs (see this figure).

Biotechnology

This is the term for the industrial application of biological systems, which are often based on micro-organisms (eg yeasts in brewing and wine-making). Excluding then long-standing application of biological wastewater treatment, biotechnology has been used within the paper industry for just a few years and mainly involves the use of separated enzymes rather than of the whole micro-organism. The presence of micro-organisms within papermaking systems is clearly not an example of biotechnology as this is causes a variety of problems.

Birch

This is a hardwood tree grown in the Northern forests and is widely used for conversion to papermaking pulp, mainly in the form of a bleached Kraft pulp. Birch has a moderate-high extractives content, which has been quoted for Betula verrucosa as 1-4% of the dry wood. The extractives in birch are composed of about 90% neutral substances (two-thirds fatty acid esters and one-third unsaponifiables) with the remaining 10% being free fatty acids (there are no resin acids in hardwoods). Birch contains no resin acids, only fatty acids. Its content of anionic substances is 250-350 μeq/g of carboxyl-containing groups compared to a glucuronic acid content of about 150 μeq/g. The accessible anionic charge is about 6 μeq/g, but this increases to about 17 μeq/g after hydrolysis due to the high proportion of esterified carboxyl groups in hardwoods.

BK

This abbreviation stands for bleached Kraft.

Blanc Fixe

This is a common name for barium sulphate, which is an important pigment used in the manufacture of photographic papers.

Bleached chemical pulps

Chemical pulps can be sub-divided into unbleached and bleached pulps, but the latter is much the larger category of the two. There are two main sub-categories of bleached chemical pulp:

- bleached Kraft pulp, which is the largest by far and the single largest type of any virgin pulp
- bleached sulphite pulp, which has been in decline for many years and is now produced in relatively small quantities.

Due to their low lignin content, bleached chemical pulps are the strongest and brightest pulps available with excellent runnability due to the low content of substances that might cause problems on the paper machine.

Bleached Kraft (sulphate) pulps

These are now the dominant bleached chemical pulp used in papermaking. They are used in many paper grades:

- in all types of graphical papers, mainly in wood-free grades, but also at a lower percentage in wood-containing grades
- in some white packaging grades such as the outer plys of folding box boards and solid bleached boards
- in premium quality tissue and towel products
- in many speciality papers such as photographic papers and artists water-colour papers.

The full process of Kraft pulping and bleaching is rarely applied to non-wood fibres, but bleached Kraft pulps are available from most of the common wood species used for papermaking, eg softwoods such as pine and spruce and hardwoods such as birch and eucalypt. In many grades of paper, but particularly the graphical wood-frees, bleached hardwood and softwood Kraft pulps are blended to give the optimum balance of strength, opacity and formation. Furnish cost is minimised by using the maximum hardwood content as softwoods pulps, being the stronger, are generally the more expensive of the two types.

The main purpose of bleaching chemical pulps is to remove the residual lignin (and extractives) as efficiently as possible and thereby maximise the pulp's strength, brightness and cleanliness (ie runnability). Consequently, bleaching gives a further yield loss of 5-7% to give an overall yield of 40-45% from the raw wood. Bleaching of chemical pulps, typically to a brightness level of around 90% ISO, is carried out in a multi-stage sequence using combinations of the following bleaching chemicals:

- chlorine (abbreviated C), which is used in the first stage of a traditional chlorine-based process to remove the bulk of the lignin
- chlorine dioxide (D), which was originally used as a partial replacement for some of the chlorine in a traditional chlorine-based process, but is now often used as the sole bleaching agent in all the non-extraction stages of an elemental-chlorine free sequence
- sodium hypochlorite (H), which used to be used in the later stages of a traditional chlorine-based process, but is now little used
- sodium hydroxide (E), which does not do any bleaching as such, but is used in the intermediate extraction stages that are present in many bleaching sequences to remove substances generated in the previous stage
- hydrogen peroxide (P), which is used (often with oxygen) to improve the efficiency of extraction stages or to provide full bleaching in its own stage (usually with or preceded by a stage with chelants)
- oxygen (O), which is used (often with peroxide) to improve the efficiency of extraction stages or to provide at least 50% delignification in what is often the first bleaching stage after Kraft pulping
- ozone (Z), which can be used, usually in a first stage, to do the bulk of delignification.

For environmental reasons associated with the generation of chlorinated organic by-products, the traditional chlorine-based sequences such as CEHDED have been largely replaced by elemental chlorine-free (ECF) processes such as OD(E_{OP})DED or totally chlorine-free (TCF) processes such as OZEP, OPP, etc. Each stage comprises a period of retention in contact with the bleaching chemical under optimum conditions of high temperature (and sometimes also elevated pressure) followed by a thickening or washing stage to remove as much as possible of the dissolved organics and residual bleaching agents before passing onto the next bleaching stage, to a final drying stage (for market pulps) or to the paper machine at integrated sites.

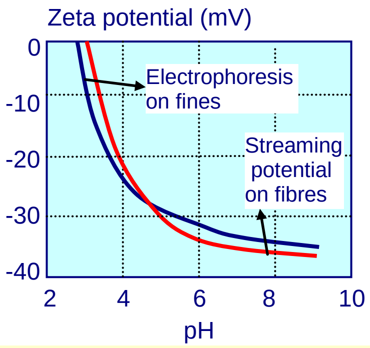
The key papermaking qualities of bleached Kraft pulps are:

- strength, which is determined largely by the pulp's physical properties (ie particle size distribution in terms of fibre length and fines content) and is little influenced by pulp chemistry (other than the absence of bulk lignin) as this is dominated by cellulose
- brightness, which is determined by the residual lignin and is well-defined as this is the main control parameter for the bleaching process
- runnability in the sense of containing the minimum level of substances that can cause problems on the paper machine, notably pitch and anionic trash in the case of bleached Kraft pulps.

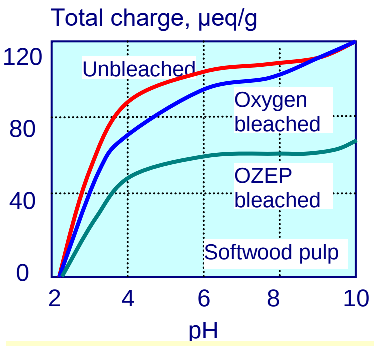
Although the extractives content of bleached Kraft pulps is low (usually < 0.5%), there is still the possibility of pitch problems on the paper machine due to the pitch-forming substances being fully ionised at papermaking pH levels (see this diagram). However, the pitch potential of bleached Kraft pulps is relatively low and is best controlled (on all except tissue grades) by the simple technique of talc addition to the pulper, the retained talc then contributing to sheet opacity. As a fine colloidal dispersion, the extractives that do remain are part of the pulp's fines fraction, which is dominated by cellulosic materials in the case of bleached Kraft pulps. The level of (primary) fines in bleached Kraft pulps is low (<10%) for both hardwood and softwoods, but refining of the pulp raises the level of fines to 10-20%. Refining is used on most machines using bleached Kraft pulps with the exception of some tissue machines due to its adverse effect on bulk and softness.

Once the pulp is slushed in water in the papermaking system, the charge characteristics of bleached Kraft pulps need careful analysis in terms of the extent to which the anionically-charged substances remain with the fibre or dissolve in the liquid phase. This is important for all pulps, but particularly so for bleached Kraft pulps due to the low level remaining in the pulp after bleaching and the relative ease of dissolution during slushing and refining because of the pulp's good swelling characteristics.

The low lignin content of bleached Kraft pulps means that their charge is virtually all due to anionic hemi-celluloses. The relationship between surface charge (potential) and the content of anionic groups in some chlorine-bleached softwood Kraft pulps is shown here. Most published data indicate that the total charge content of bleached Kraft pulps is below 50 μeq/g for softwoods and in the range 50-100 μeq/g for hardwoods. For all pulps, the measured surface charge becomes more negative with increased pH due to ionisation of carboxyl groups, there being a similar charge on both the “fibre” and fines fractions, as shown in the figure at right above (which is almost certainly for an older-style chlorine-bleached pulp).



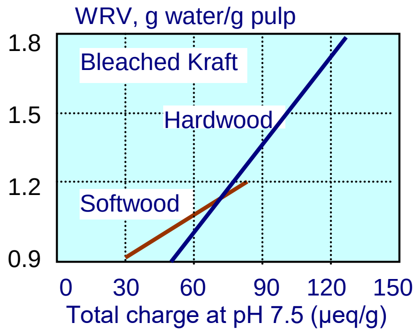
Source: Jaycock and Pearson, J.Colloid Interface Science, 1976, 55, 1, 181.



Source: Laine, J in Paperi ja Puu, 1997, 79, 8, 551-559.

More recent data for softwood TCF pulps (see figure at left) shows a similar trend of increasing measurable total charge as the pH gets higher. The still-increasing charge at pH 10 suggests some contribution from ionisation of phenolic hydroxyls. The total charge content at papermaking pH levels (pH 6-8) for the fully-bleached pulp is comparable with data from other sources for both ECF and TCF bleached Kraft pulps. It is also evident that there is substantial removal of anionic groups by the ozone (Z) bleaching stage.

Due to their low lignin content, bleached Kraft pulps have good swelling characteristics. There is a good correlation between swelling (water retention value) and total charge content (as shown in the figure at right). This indicates that the swelling of hardwoods increases more with increased charge than it does for softwoods. This could be due to the thinner cell wall of hardwoods (particularly of the birch pulps used here) compared to softwoods. The impact of refining these hardwood pulps (data shown here) was to double both the fines content and the measurable surface charge of each pulp.



Source: Laine and Stenius in Paperi ja Puu, 1997, 79, 4, 257-266.

Further data on the content of charged substances in bleached Kraft pulps is shown here in terms of the effect of pH on swelling and here for the total charged substances determined by various types of charge titration; there are also several examples covered under ECF pulps and TCF pulps. Some useful data on a range of softwood and hardwood pulps is also shown in the table below. The highest charges are for those TCF pulps bleached with oxygen and/or peroxide, which is due to their inability to remove the hexenuronic acid content of the pulp. The fines contents of the pulps was typically low (7-8% for hardwoods and 3.5-5% for softwoods), so removal of fines only had an impact on charge at high charge contents. The surface charge of all pulps was about 20% of the total charge, but higher proportions (about 40% of total) have been measured on other TCF pulps (see here) and ECF pulps (see here).

CHARGE CHARACTERISTICS OF ECF AND TCF KRAFT PULPS

Pulp	Bleaching Chemicals	Total charge (μeq/g)		Surface charge (μeq/g)	
		Fibre + fines	Fibre only	Fibre + fines	Fibre only
TCF HW	OZP	47	47	10	9
ECF HW	D	53	50	10	9
ECF HW	D	58	55	11	10
TCF HW	OP	95	94	17	14
TCF HW	OP	127	129	27	22
TCF SW	OZP	35	33	6	6
ECF SW	D	40	42	8	7
TCF SW	OZP	59	58	13	12
TCF SW	OP	68	69	14	12
TCF SW	OP	85	84	16	13

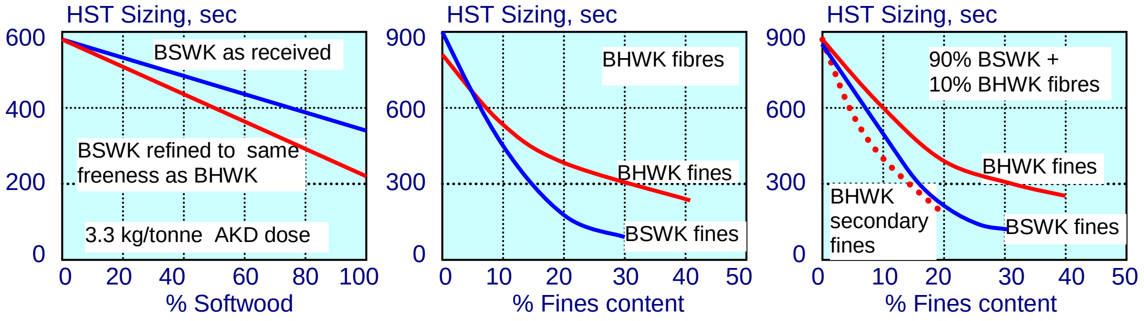
Note: Total charge from titration with low molecular mass ionene polymer and surface charge from titration with high molecular mass polydadmac polymer (see charge titration for further discussion of this)

Source: Laine and Stenius, Paperi ja Puu, 1997, 79, 4, 257-266.

As seen above, the characteristics of bleached Kraft pulps do vary considerably depending on the nature of the wood type and of the final bleaching stages. These differences are carried forward into the product, one particularly important aspect being their response to wet end sizing agents (see this example for comparison of AKD sizing of an unbleached and bleached Kraft pulp).

Pulp	Fines (%)	Fines area	WRV	Turbidity	Cationic demand	Hemi-celluose (%)		Lignin (%)	
	In refined pulp	(m^2/g)	(g/g)	(FTU)	(μeq/g)	Fibre	Fines	Fibre	Fines
Softwood	8	10.6	2.5	4060	7.5	0.3	1.8	20.4	24.5
Hardwood	18	4.5	2.1	2330	33	0.3	2.7	22.3	29.5

Source: Ramamurthy, J.Pulp Paper Science, 2000, 26, 2, 72-75.

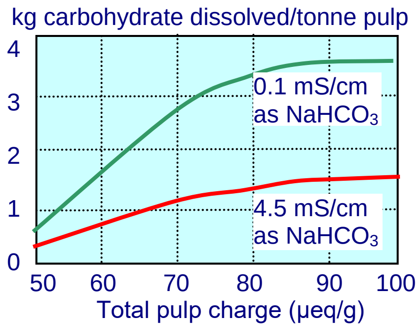


Wood-free fine papers are most commonly made from a blend of bleached hardwood and softwood Kraft pulps, typically in about a 2:1 ratio, but the balance can vary with grammage (eg less softwood pulp as the grammage rises). A study using two well-characterised bleached Kraft pulps (see table above) has shown how certain pulp attributes influence the sizing efficiency for a cationic starch-emulsified AKD size (3.3 kg AKD/tonne pulp dose).

The difference between the sizing of bleached softwood (BSWK) and hardwood Kraft (BHWK) pulps is clearly demonstrated in the first figure above at left, where the sizing deteriorates progressively with a higher proportion of softwood. The refined BSWK pulp has a greater impact on the loss of sizing than the as-received BSWK pulp and the middle figure above shows that the fines from BSWK are more deleterious than BHWK fines. The AKD retention was similar (23-27%, giving about 0.8 kg AKD/tonne paper) across all the handsheets (which were made without retention aids), indicating that the most likely explanation for these effects is the different specific surface area of the fines (see above table). The fines in all these examples was a mixture of primary and secondary fines as the samples were obtained from a paper mill after refining. The right-hand figure indicates that BHWK secondary fines are comparable with BSWK mixed fines in terms of reduced sizing and significantly more deleterious than primary BHWK fines. These results have important implications for pulp treatment at paper mills:

- ❑ the need for good refiner control so as not to over-refine any pulp
- ❑ the need for separate refining of BHWK and BSWK pulps (as is often, but not always, practised) so as not to over-refine unnecessarily the BHWK pulp.

The dissolved solids content of bleached Kraft pulps is lower than other pulps (usually < 1%) simply because most of the potentially-soluble materials have been dissolved and removed from the pulp during bleaching. The dissolved solids that do remain in the pulp are a mixture of residual bleaching chemicals that give rise to some pulp-derived conductivity and dissolved organics (mainly hemi-cellulose carbohydrates). Because of the tremendous change in bleaching chemistry since the early 1990s, great caution is required in interpreting published data on the characteristics of dissolved solids in bleached Kraft pulps as most of the data prior to this time will be for older-style chlorine-bleached pulps. Data on dissolution from ECF and TCF bleached Kraft pulps are shown in those sections.



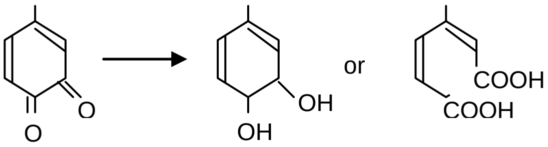
Pulps refined at 100 kWh/tonne at 3.5%, pH 7.5

Reference: Sjostrom et al Nordic Pulp Paper Research J, 2000, 15, 5, 469-475.

When pulps are refined after slushing, further dissolution takes place as the fibrous structure is opened up by the mechanical action. At any refining level, the dissolution is determined by a combination of the pulp's total charge content and the electrolyte level in the water. This is shown at left for a number of refined hardwood and softwood ECF and TCF pulps of differing charged contents. Further examples of the effects of refining on dissolution of organics from TCF bleached Kraft pulps are given in the refining section.

Bleached mechanical pulps

With increasing pressure on the brightness of wood-containing papers, bleaching of mechanical pulps is becoming more common, although this may be seasonal rather than all-the-year-round. The bleaching of mechanical pulps is sometimes referred to as pulp brightening as the intention is not to remove the lignin, but to change its structure to a less-coloured form. This change is usually attributed to the reduction of quinoid structures in lignin to phenolic groups or oxidation to carboxyl groups as shown at right.



There are two main bleaching/brightening chemistries for mechanical pulps:

- oxidative bleaching with hydrogen peroxide operating under alkaline conditions.
- reductive bleaching with sodium hydrosulphite operating at slightly acid pH.

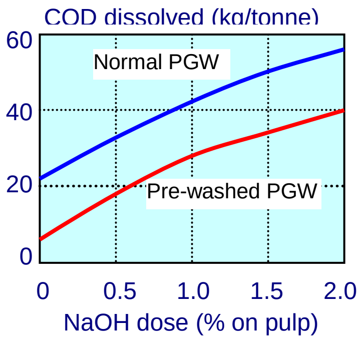
Both processes use auxiliary chemicals such as sodium silicate and chelants to maximise the activity of the bleaching agent through minimising their decomposition reactions. The ISO brightness of the mechanical pulp can be increased from 50-70% before bleaching to around 80% with a 2-stage peroxide bleaching process, but this brightness level is no more stable than that of an unbleached pulp due to the problem of brightness reversion.

Apart from raising the pulp brightness, hydrosulphite bleaching has little impact on the chemical character of the bleached pulp, but peroxide bleaching brings about two significant changes:

- the alkaline conditions of peroxide bleaching lead to significant dissolution of wood substances (loss of yield) and to potentially high quantities of dissolved solids in the resultant pulp
- the oxidising action of peroxide leads to the introduction of new anionic groups, which may be useful in papermaking if the charged substances remain associated with the fibre, but become a problem if they dissolve in the papermaking system and then contribute to anionic trash.

Bleaching of spruce TMPs with hydrogen peroxide leads to hydrolysis of the acetyl (CH_3CO) groups on the galactoglucomannan hemi-celluloses and dissolution of up to 20 kg acetic acid/tonne pulp. This deacetylation reduces the solubility of the galactoglucomannans so that they are re-deposited on the fibres, but this loss of solubility also destabilises colloidal pitch particles. One example quotes a reduction of 75% in dissolved glucomannans (from about 8 to 2 kg/tonne pulp) after peroxide bleaching. The pectin substances in the wood (many of which are present as methyl esters) are also hydrolysed, but in this case to the more-soluble acid, one example quoting a 4-fold increase in dissolved galacturonic acid on peroxide bleaching (from about 1 to 4 kg/tonne pulp). The cationic demand of the peroxide-bleached pulp was also about 4x that of the unbleached pulp.

The impact of the dose of caustic soda on organics dissolution in peroxide bleaching (1-3% doses on pulp) is illustrated at right for a pressurised groundwood (PGW) pulp. This shows a progressive increase in dissolved COD with NaOH dose. Increasing the peroxide dose improves pulp brightness, but has little impact on dissolution. The benefits of pre-washing the pulp before bleaching is evident from the significant difference between the two lines. This study also showed a good correlation between COD and dissolved cationic demand, the latter increasing to about 100 μeq/g at the highest NaOH doses. The reasons for the increased anionic character on peroxide bleaching of the PGW pulp is the same as for TMPs described above, ie alkaline hydrolysis of existing methyl esters plus oxidation of lignin entities to form carboxyl groups. In both cases, there may also be a contribution from any added sodium silicate.

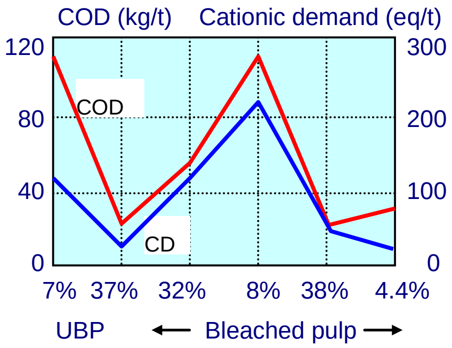


Source: Brauer et al in Pulp Paper Canada, 2001, 102, 4, 44-48.

Other studies have confirmed that hydrosulphite bleaching has no effect on the level of anionic substances in the pulp and also provided further data on the level of charged substances from peroxide bleaching:

- data in this table indicates an approximate doubling of total anionic substances on bleaching a spruce TMP (from about 90 to 180 μeq/g)
- the total anionic charge of a spruce TMP approximately doubled on bleaching, from about 80 to 175 μeq/g for one pulp's fibre fraction and from 140 to 350 μeq/g for its fines fraction.
- the total charge of a pulp increased from 90 to 290 μeq/g on bleaching with the dissolved material accounting for 20 μeq/g (22%) of the total charge in the unbleached pulp and 80 μeq/g (28%) in the bleached pulp.

Because of the increased dissolution during peroxide-based bleaching, the installation of a bleaching stage at a mechanical pulp mill often includes a more efficient washing stage after bleaching. The example at right shows the profile for cationic demand (CD) and dissolved organics (as COD) from a stone groundwood pulp as it passes through a peroxide bleach plant. The first thickening stage lowers the organics in the unbleached pulp (UBP) in line with the increased consistency. Bleaching contributes a further 30 kg COD/tonne pulp and 80 eg CD/tonne (80 μeq/g), which agrees with the figure quoted above. Dilution of the bleached pulp increases the COD and CD due to the organics in the dilution water and final thickening lowers the COD to about 20 kg/tonne pulp and the cationic demand to below 20 eq/tonne for passing to the paper machine. The actual variation in the cationic demand on a newsprint machine using a mixture of unbleached and bleached TMP is shown here.



Source: Brauer et al in Pulp Paper Canada, 2001, 102, 4, 44-48..

Bleached sulphite pulps

In view of their limited production and use in papermaking today, these are discussed briefly under sulphite pulps.

Bleaching

This is the process of improving the whiteness or brightness of a papermaking pulp so that it is compatible with the grade of paper being made. The process of bleaching may be applied to all types of pulp - virgin mechanical pulps, virgin chemical pulps, deinked pulps and, in some cases, to machine broke (albeit the latter is more decolorising than bleaching). In each case, the mechanism is different and this is described further under each pulp heading.

Bleaching chemicals can be divided into two broad categories:

- ☐ the oxidising bleaches
  - chlorine gas and/or sodium hypochlorite, which are much used less commonly used today than then they were, notably for virgin chemical pulps, due to the well-known issues related to the generation of undesirable chlorinated organic by-products. Sodium hypochlorite is also sometimes used for bleaching broke.
  - chlorine dioxide, which is used predominantly for the bleaching of virgin chemical pulps
  - oxygen, which is used for bleaching of virgin chemical pulps and wood-free deinked pulps
  - ozone, which is used for the bleaching of virgin chemical pulps
  - hydrogen peroxide, which is used for the bleaching of virgin mechanical and chemical pulps and of deinked pulps
- ☐ the reducing bleaches
  - sodium hydrosulphite, which is used for the bleaching of virgin mechanical pulps and deinked pulps
  - formidine-sulphinic acid, which is used for the bleaching of deinked pulps.

Board

This is a very generic term for products that exceed a certain thickness (usually 0.3mm) or a certain grammage (about 250 g/m^2). However, the term is used very loosely as some products with values below these criteria are often referred to as boards, eg linerboard. Other than those board grades used for packaging, there are a number of other board products such as plasterboard where the board forms the outer barriers for the plaster sandwich.

BOD

This is an abbreviation for biochemical oxygen demand.

Bond

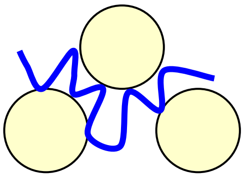
This term may be used in many circumstances, but there are two main ones in papermaking:

- ☐ bonds within chemicals which are described under chemical bonds
- ☐ inter-fibre bonds, which are due to hydrogen bonds between cellulose molecules, but the overall bond strength also depends on the conformability of the bulk fibres.

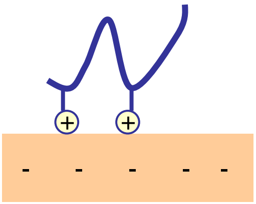
Borate

Boron is the lead element in Group 13 of the Periodic Table, but is not commonly found in papermaking systems. The most common salts of boron are the borates, notably borax - $Na_2B_4O_7.10H_2O$. Borates can be present in papermaking systems using recovered paper through the use of borax as a cross-linking agent with starches used as adhesives in the manufacture of corrugated cases. Sodium borohydride is used to generate sodium hydrosulphite.

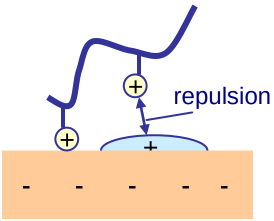
Bridging



As shown in the general picture at right, bridging is a type of aggregation process for fine particles brought about by certain types of polymer. This is one of the various types of fine particle aggregation that is often referred to as flocculation. Aggregation by bridging is brought about by polymers that are initially adsorbed on one particle, but are able to contact the surface of a nearby particle via the polymer loops that protrude from the surface (see this more detailed figure). This type of adsorption is most likely to occur for high molecular weight polymers having a low-moderate charge density in the presence of an oppositely-charged concentrated suspension.

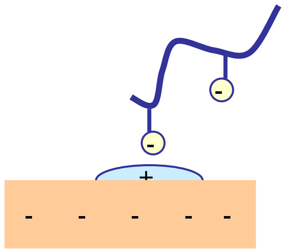


The polymers that work predominantly by this mechanism are anionic or cationic polyacrylamides because of their high molecular weight and extended chain conformation that allows them to bridge the gap between particles. In the case of cationic polyacrylamides and the normally-anionic particles, the electrostatic attraction provides a driving force for initial adsorption (see picture at right), but, if this was too strong, the polymer would adopt a flatter conformation on the particle surface and bridging would be unlikely. The level of charge attraction is optimised through selecting a polymer with the correct balance of cationic charge density and chain length (molecular weight).



Cationic bridging polymers are sometimes used as part of a dual component system, where the other component may be a different sort of cationic polymer. The second polymer is likely to be a lower molecular weight, more highly-charged polymer (eg polydadmac or PEI), which is added first to create cationic patches on the anionic particle surface (see picture at left). The presence of such patches can promote inter-particle attraction in its own right, but, when they are used with cationic bridging polymers, the patches prevent the adsorption of segments of the cationic polymer chain and promote the more extended chain conformation needed for effective bridging. This type of "blocking" action or co-operative activity between different polymers is utilised in the action of colloidal silica with polyacrylamides and is particularly valuable in systems with high levels of electrolytes, which reduces the chain extension of charged polymers. (It should be noted that electrolytes also reduce the width of the electrical double layer around colloidal particles and the deliberate addition of electrolytes is sometimes used [but never in papermaking] to allow bridging by shorter-chain polymers, a process which is called sensitisation.)

It is also possible to use bridging polymers with the same charge as the particle surface, but this normally requires the use of a cationic substance to act as a link between the anionic particle and the anionic polymer (see picture at right). The cationic material could be a multi-valent cation such as calcium or alum/PAC or a low molecular weight, highly-charged cationic polymer similar to those used in a "blocking" mode with cationic bridging polymers described above. This approach is particularly useful when the system contains a high level of cationic material that is essential for some other functional effect (eg wet strength), where the particle surface may be fully cationic due to the high addition rate required. An example of the reflocculation ability of a dual polymer system with an anionic polyacrylamide and polyethyleneimine is shown here. The use of anionic starches with PAC is another example of this type of system, although inter-particle bridging is not the aim in this case.



Brightener

This is short-hand for fluorescent brightening agent.

Brightness

This is an important optical property of some papers, which is similar to, but not the same as, whiteness. It is relevant to many paper grades, but mainly to those destined for printing such as most wood-free and wood-containing papers and some packaging grades. The brightness of a paper is critically dependent on the brightness of the pulp plus the level and types of any filler or fluorescent brightener added. The brightness of paper is measured as the ratio of the reflectance of the paper when illuminated by blue light at a wavelength of 457nm compared to the reflectance of a magnesium oxide standard. It is usually expressed as a percentage rather than as a fraction, but is also sometimes expressed in degrees or points. It is a directional measurement with illumination of the paper surface at 45^{o} and observation at 0^{o} (ie normal to the surface).

The brightness of pulps varies widely, but ISO values are typically 15-30% for unbleached Kraft, 50-70% for mechanical pulps (depending on the degree of bleaching) and at least 88% for bleached chemical pulps. The brightness of finished papers varies from about 55-70% for newsprint, through 65-72% for SC and 70-78% for LWC papers to at least 90% (and sometimes over 100% where high fluorescent brightener levels are being used) for wood-frees. Typical brightness levels for the main fillers are shown in the table at right.

Filler	ISO brightness (%)
Limestone	90-93
Marble	94-95
PCC	96-97
Talc	81-90
Kaolin clay	82-88
Calcined clay	90-92
Titanium dioxide	97-98

Brightness reversion

This is the process (sometimes referred to as "yellowing") where a mechanical pulp or, more typically, a wood-containing paper loses some of its original brightness and becomes darker over time when exposed to ultra-violet light. This is due to the oxidation of lignin compounds, notably the introduction of carbonyl (C =O) groups and is believed to be caused by hydroxyl free radicals. Attempts have been made to suppress this effect using inhibitors such as vinylpyrrolidone and its polymers.

Britt Jar

This is an alternative name for the dynamic drainage jar, named after its developer, the late Ken Britt of the Empire State Paper Research Institute (ESPRI) at the University of Syracuse in New York state.

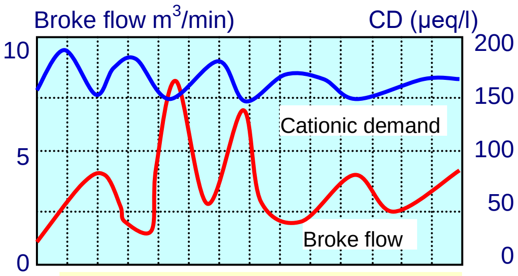
Broke

This is the papermaker's term for non-saleable product due to the paper not conforming to its specification, ie unacceptable quality. There may be numerous reasons for this, but they can be broken down into two types:

- not meeting the required specification for one or more parameters (such as grammage, sizing level, etc) throughout the manufacturing run, which is likely to be caused by some fundamental problem (eg an incorrect pump setting or a retention-related problem)
- a lack of uniformity within one or more reels, which is likely to be caused by variability somewhere in the system.

In nearly all cases, broke is returned to the papermaking system after a period of storage, which ranges from a few hours to several weeks. Broke is a form of non-deinked recycled pulp (in the sense that it is usually returned with no chemical treatment), but one with the significant advantage that it is (or should be when managed properly) of known chemical composition. By re-using broke on identical or similar grades, the recyclability of all its components, not just the fibre, can be maximised.

The type and quantity of broke may have a very significant impact on the paper machine's wet end chemistry, but this depends on the grade of paper being made. The most significant impacts occur when the paper is being surface-treated either at the size press or by coating, as the surface-added chemicals are not designed to be effective at the wet end and may have detrimental effects. Broke that does not contain surface-added chemicals may be "cleaner" (in the sense that it contains less problematic substances) than the fresh pulps, although this does depend on the type of fresh pulp and the machine's degree of water closure (as this affects the retention of dissolved solids). An example is shown at right for a 100% deinked newsprint machine, where an increased broke flow shows a good inverse correlation with the cationic demand (CD) of the mixed (broke and deinked pulp) stock for papermaking. Unfortunately, this beneficial effect of broke recycling is not as common as the converse.



Source: Gill, R at Papex Awards 2001.

The most serious adverse effects from broke recycling are due to:

- size press starches, which, with the exception of cationic types, are weakly held by the fibre and thus contribute to the dissolved solids entering the wet end. A machine re-using 20% broke that contains 5% starch (a not-atypical level for many papers) returns to the wet end a starch load of 1% (on paper production), but the significance of this depends on the grade being made. For fine paper machines using bleached chemical or deinked pulps, the broke is likely to be the biggest source of dissolved solids (mainly organics) at the wet end. For packaging machines using recycled (non-deinked) pulp, the broke-derived organics are less significant as the recycled pulp could itself contain up to about 5% starch. The main adverse effect from the return of such size press starches is the well-known range of microbiological problems, but other effects such as impaired drainage and a contribution to anionic trash are also possible.

- fluorescent brightening agents (FBAs), which, when added at the size press, are likely to be of the more water-soluble tetra- or hexa-sulphonated type. The unmanaged return of such broke could cause significant product quality problems, but the fluorescence can be controlled by addition of quenching chemicals. Being highly anionic and water-soluble, such brighteners also contribute to anionic trash levels.
- dispersants present in coating pigments and/or added to the coating formulation. These represent a problem at the wet end as they tend to be highly anionic (such as the polyacrylates) and thus contribute to the interfering anionic trash fraction (see this example).
- latex from coated broke leading to the possibility of problems from white pitch.
- dyes are generally added at the wet end, so should be reasonably well-retained with the particulate matrix when coloured broke is recycled. However, when the return of coloured broke is not positively managed and is made to grades of different colour, the broke requires bleaching. Although this gets rid of the colour incompatibility, such treatment is likely to be more efficient in dissolving substances from the broke than simple repulping and is thus generally undesirable from a wet end chemistry perspective.
- wet strength resins are generally added at the wet end, but wet strengthened broke cannot be used without special treatment as it does not readily disperse into separate fibres. Special treatment is thus inevitable, but is facilitated by recycling the broke as quickly as possible.

It is evident that many of the surface-applied chemicals that reach the wet end through broke recycling cause problems of one sort or another. It is thus paramount that broke production is minimised, not just because of the raw materials that are irrecoverably lost, but because of these adverse effects on wet end chemistry which then adversely influence productivity and product quality.

As with all substances that cause problems, these are best prevented at source by using materials that cause no or less severe wet end problems and, if this is not possible, by trying to stop the recycled substance express this undesirable effect. For water-soluble substances, the simplest way is to thicken or wash the repulped broke before mixing it with the rest of the papermaking stock.

Bromine

Like chlorine, this element belongs to the halogen group (17) of the Periodic Table, but has a much higher molecular mass (79.9). It exists as a brown liquid (Br_2) at ambient temperatures, but is not supplied or used in this form at paper mills.

Bromine is present in the following raw materials, all of which are used to control some aspect of the microbiology within the papermaking process:

- sodium bromide, which is used to generate sodium hypobromite
- organic bromine- (and chlorine-) release compounds such as BCDMH
- ammonium bromide, which is used with sodium hypochlorite
- other organo-bromine compounds.

Brownian motion

This motion is possessed by all particles due to their inherent thermal energy. From the kinetic theory initially developed for gases, all molecules and particles posses, in the absence of an external force, a translational kinetic energy which is equal to 1.5kT where k = Boltzmann's constant = 1.38 x 10^{-23} Joule/^{o}K and T = temperature (^{o}K). The fact that the energy is the same for all particles (irrespective of their size) means that the attainable velocity gets progressively smaller as the particle size increases and is thus insignificant for particles greater than about 1μ in size. Brownian motion is responsible for the process of diffusion and for the perikinetic aggregation of particles.

Bulk

This term is used to denote the specific volume of paper in units of cm^3/g, which is simply the reciprocal of the sheet density.

Burst strength

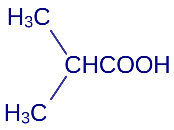
This strength parameter is the paper's resistance to puncture and is measured, most commonly in a Mullen-type tester, by pressuring a constrained paper sample via an air-inflated membrane until it ruptures. Burst strength is expressed as a pressure (kPa) or in a normalised form as the burst factor or burst index where the burst strength is divided by the grammage (kPa.m^2/g). The value of burst strength reflects the average MD/CD tensile strength of the paper and its MD elongation at failure.

Butyric acid

This is one of a number of simple organic acids that can be generated within the papermaking system by certain types of acid-producing bacteria. The acid exists in two isomeric forms as shown at right.

Normal (n-) butyric acid - $CH_3CH_2CH_2COOH$

Iso-butyric acid



Calcined clay

When kaolin clay is heated at high temperature (calcined), the water of hydration is removed and the platelets fuse in a face-to-face configuration. This produces a bulky clay with a high void content and thus excellent light scattering ability (see this table for characteristics of calcined clay versus ordinary clays).

Calcium

Calcium (Ca) is the second element of the alkaline earth metals (Group 2 of the Periodic Table) and has an atomic mass of 40. It is a very common element in papermaking systems, occurring in three possible forms:

- ❑ calcium carbonate minerals, which are widely used as wet end fillers and coating pigments
- ❑ calcium sulphate minerals, which are used as coating pigments, but this practise is not common
- ❑ as a dissolved cation, most commonly associated with either bicarbonate or sulphate anions. The main sources of dissolved calcium are:
    - the hardness salts naturally present in fresh water
    - dissolution of calcium carbonate under acidic conditions at the wet end
    - dissolution of calcium sulphate from coated broke.

In papermaking systems, calcium is deliberately present only in a particulate form as calcium carbonate (or calcium sulphate), but dissolved calcium is a very important cation at the wet end for several reasons:

- ❑ it can be held as the counter-ion by the anionic charges on particulate surfaces, which has several consequences:
    - reduction in the adsorption of cationic additives on pulp/filler (see example here for a cationic polyacrylamide, here for a cationic starch and here for a PAE resin)
    - enhancement of the adsorption of anionic additives such as dyes (see this example) and brighteners (see this example)
    - impaired swelling of pulp fibres and loss of strength potential
    - reduced dissolution of organics from pulps (see this example for an unbleached Kraft pulp)
- ❑ it can be precipitated, most commonly as the carbonate, but also sometimes as the sulphate or oxalate, thus contributing to general deposits and/or scale.
- ❑ it contributes to general electrolyte levels and their attendant (usually undesirable) effects.

As with all soluble ions, the dissolved calcium concentration on the paper machine depends on its input load and the degree of water closure (see these values for several machines with fully-closed water systems). It is evident from the above list that dissolved calcium has both positive and negative effects at the wet end of paper machines. Putting aside the few rather special cases where calcium sulphate is used as a pigment, dissolved calcium is, on balance, undesirable and, so far as this is practicable, its presence should be minimised. Where its level cannot be reduced, its potential advantages in terms of using additives in an anionic rather than a cationic form (eg anionic starches) should be fully explored.

The form of the dissolved calcium is important only in relation to its tendency to precipitate as calcium carbonate, which arises only when it is accompanied by the bicarbonate anion. This happens when it is present in fresh water as temporary hardness and when it is dissolved from calcium carbonate by carbon dioxide, which occurs mainly through microbial activity. The latter is a major problem on some paper machines, notably those operating substantially closed water systems. In such cases, control of microbial activity is one of the best ways to minimise dissolved calcium concentrations.

Because of these effects, it is important that the concentration of dissolved calcium within the wet end is regularly monitored. In the dissolved state, this can be done simply by EDTA titration at alkaline (>11) pH, where any magnesium is precipitated prior to titration. Alternative techniques include ion chromatography and specific ion electrodes.

Calcium bicarbonate

This is one of the main forms of dissolved calcium present in the papermaking system and has two possible sources:

- temporary hardness in the fresh water
- dissolution of calcium carbonate through interaction with carbon dioxide as shown below:

$$CaCO_3 + H_20 + CO_2 \leftarrow\rightarrow Ca(HCO_3)_2$$

As discussed under calcium generally, dissolved calcium associated with any anion is, on balance, undesirable at the wet end and calcium bicarbonate has the further disadvantage that it may precipitate as calcium carbonate, which may then deposit as an attached scale. It is quite possible for calcium carbonate to dissolve in one part of the papermaking system (for example, due to microbially-generated CO_2 from slimes) and then re-precipitate in another, where the chemistry is less aggressive.

The presence of calcium bicarbonate in fresh water is important to the use of fresh water on wet end showers. The heating and pressurisation of shower waters changes the equilibrium position of the reactions influencing the stability of calcium carbonate and this may lead to precipitation around the shower head or within the formation fabric or press felt. There are several techniques available to reduce the water's tendency to precipitate calcium carbonate under such circumstances:

- pH adjustment

  The pH at which the precipitation reaction is at equilibrium can be calculated from Langelier's equation for situations where the system is closed to the atmosphere (ie no exchange of CO_2). The pH of the water can then be adjusted accordingly.

- convert hardness to a permanent form

  This is done simply by acidification, but care is needed to ensure that the new anion (eg sulphate from sulphuric acid) does not bring its own set of problems.

- treatment (conditioning) of the water with an electromagnetic field

  This technique is widely used, but its efficacy is not easily predictable.

- chemical conditioning of the water

  There are two different approaches:

  - the addition of chelants such as EDTA, DTPA and polyphosphates, but, as these require stoichiometric doses, they are not usually cost-effective.
  - by the addition of chemicals that interfere with the crystallisation process, examples being organo- phosphonates and specific anionic polymers.

Calcium carbonate

Calcium carbonate ($CaCO_3$) is a very common material in many papermaking systems, where it is used for two main purposes:

- ❑ as a wet end filler at levels up to about 30% of the paper content
- ❑ as a coating pigment at levels up to about 90% of the coating layer.

It is also sometimes used at much lower addition levels (about 1% on pulp) for pH control and, in this case, the calcium carbonate dissolves and releases calcium ions into solution and generating carbon dioxide gas, as shown below.

$$CaCO_3 + 2H^+ \leftarrow\rightarrow Ca^{2+} + H_2O + CO_2$$

Calcium carbonate added as a filler or pigment can also dissolve incidentally at the wet end by reacting with mineral acidity (as above) or by reacting with local acidity (for example, that generated in situ by microbiological activity). The calcium thus dissolved might re-precipitate, perhaps in a different physical form, in another part of the papermaking system where the water chemistry is different. It is also possible that dissolved calcium from other sources (eg temporary hardness in the fresh water) could precipitate as calcium carbonate if the water is not at chemical equilibrium. If precipitation occurs within the papermaking stock, this causes no real problems, but it can sometimes occur within machine fabrics or as a scale on the surface of pipes and spray-heads, in both cases causing blockage problems (see calcium bicarbonate for discussion of the techniques to prevent this).

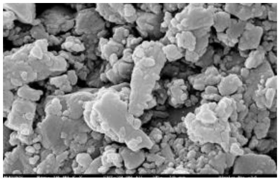
The dissolution of calcium carbonate under acid conditions limits its practical use to systems where the pH exceeds about 6.5. In pure water (ie no other materials present), the solubility of carbonates is determined only by the partial pressure of carbon dioxide, which gives an equilibrium concentration of about 20 mg/l (as dissolved Ca) for calcium carbonate at pH 8.4. In the presence of other neutral electrolytes, the solubility of calcium carbonate increases and might double to around 40 mg/l (as dissolved Ca) in the most concentrated papermaking systems. Under more alkaline conditions, its solubility decreases due to the increased ionisation of bicarbonate to carbonate. Temperature has a negative effect on carbonate solubility due to the reduction in equilibrium carbon dioxide levels with the solubility at 50^oC being about 13 mg/l (as dissolved Ca) in electrolyte-free water. These issues related to calcium carbonate instability are relevant to wet end chemistry, but rarely to the use of calcium carbonates in coating.

Calcium carbonate occurs naturally in two main crystalline forms – aragonite and calcite with the latter being the most stable and therefore predominating in most of the natural minerals. Calcite has a basic trigonal structure, but this can be combined in different ways to give an enormous variety of crystal forms (see pictures below).

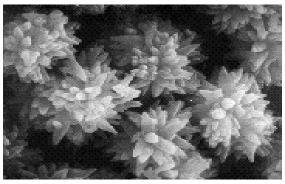
Calcium carbonates are reckoned to account for about 4% of the Earth's crust and occur naturally in various forms, the main ones being:

- ❑ limestone, which is a sedimentary material originating from both biological (the skeletal remains of marine organisms) and chemical processes
- ❑ chalk, which is a sedimentary material derived solely from animal/plant remains and is much softer than limestone
- ❑ marble, which is a hard, coarse, metamorphic form of limestone/chalk.

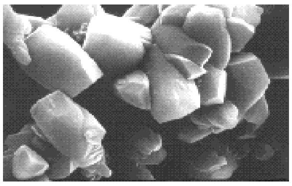
GCC



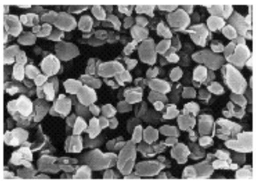
Scalanohedral PCC



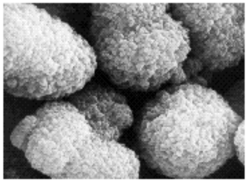
Rhombohedral PCC



Prismatic PCC



Spherical PCC



All three minerals are used in papermaking with limestone and chalk being the most widely-used. All the natural carbonates have a high purity and are manufactured simply by classification and, in some cases (eg for the harder marbles and limestone), by grinding to give commercial products with a defined particle size distribution. The density of all calcium carbonates is 2.7 kg/dm^3 and refractive index 1.58, but the papermaking properties of calcium carbonate fillers vary with type and grade as summarised below for some typical products.

Filler	Brightness	Light scattering	Particle size distribution (%)				Surface
	(ISO, %)	coefficient (m^2/kg)	>10μ	<2μ	<1μ	<0.5μ	area (m^2/g)
Chalk	81-85	150	5	45	25	10	3
Limestone	90-93	-	1	60	35	-	7
Marble	94-95	-	0-1	60-95	35-80	20-65	7-15
PCC, scalanohedral	96-97	220-290	0	80	50	17	7-12
PCC, prismatic	-		0	95	80	-	10
PCC, rhombohedral	-		0	100	80	-	8

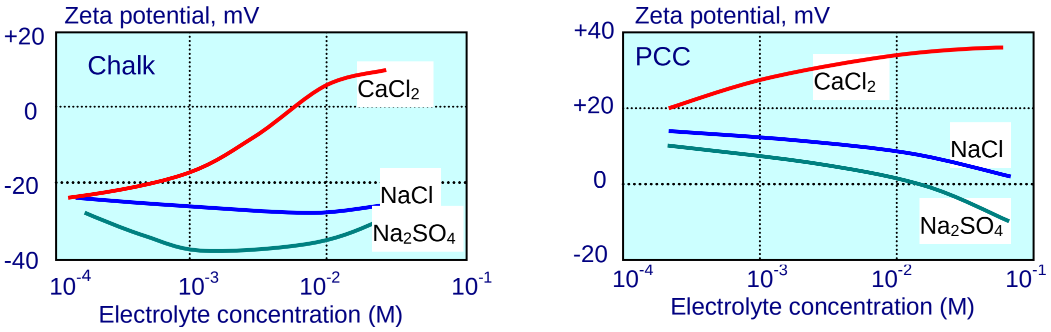
Calcium carbonates account for about half of global mineral use for filling and coating, but for well over half of total filler use in Europe. The major trend in mineral use over the last 30 years has been the swing away from kaolin clay to calcium carbonate and, over the last 10 years, the fracturing of the carbonate market between the traditional natural carbonates and the synthetic precipitated calcium carbonates (PCCs). The latter account for about one third of global calcium carbonate use in papermaking, but, in North America, PCC accounts for about 80% of total carbonate use. The reasons for the rise of calcium carbonate are now well known as listed below:

- in Europe, the slightly lower cost of natural carbonates than clay and, in North America, the much lower cost of PCC compared to the more prevalent titanium dioxide
- higher natural brightness, particularly for the ground marbles and PCCs, which are brighter than fully-bleached chemical pulps
- stronger, more durable fibres when paper is made at neutral/alkaline pH (an inherent feature of carbonate use due to its solubility under acid conditions) rather than at the acid pH regime that tended to accompany the use of clay
- greater sheet permeability and easier water removal from the web at the machine wet end due to the more rounded shape of carbonates compared to the platy clays
- in coating applications, the less glossy, more matt finish imparted to the coated sheet by calcium carbonate compared to clay.

The above attributes that calcium carbonates bring to papermaking have nothing, per sec, to do with their actual chemical constitution. However, when calcium carbonates are used within a pulp-based furnish as fillers at the wet end or within the pigment-dominated coating suspension, their interactions with other materials are strongly influenced by their surface chemistry.

The surface chemistry of calcium carbonate is determined largely by the adsorption of materials from solution. In the absence of such materials, the surface charge is determined by the adsorption or dissolution of calcium and carbonate ions with a predicted isoelectric point around pH 8.4. Below this pH, the charge should be positive, but the adsorption of anions from electrolytes often makes the measured charge negative at normal papermaking pH levels. The influence of three different electrolytes is illustrated in the two examples shown below for a natural chalk (about 95% $CaCO_3$) and a PCC (close to 100% $CaCO_3$). The chalk is anionic in deionised water and in the presence of high low-high concentrations of sodium chloride and sulphate. In the presence of calcium chloride, however, there was strong calcium adsorption with charge reversal occurring at about 400 mg/l dissolved Ca. Although the purer PCC is cationic in deionised water, it is still able to adsorb further calcium from solution, but the charge can also be reversed at high concentrations of neutral sodium salts.

These significant differences in surface charge would affect the adsorption of additives such as cationic starch in a system when only these two materials are present. However, in a papermaking system in the presence of pulp, the surface chemistry and charge of the fillers is changed by the presence of substances (such as anionic hemi-celluloses) that have dissolved from the pulp (see these examples for other mineral particles).



Source: Hedborg in Nordic Pulp Paper J., 1993, 3, 319-

Calcium oxalate

This is a precipitate (CaC_2O_4) that may be formed in papermaking systems using sulphite pulps as oxalic acid is produced in this pulping process. The precipitate is more common in the pulping system, but oxalate ions may be carried over with the pulp depending on the pulp washing efficiency.

Calcium stearate

The calcium soap of stearic acid $(C_{17}H_{33}COO)_2Ca$ is used in an emulsion form as a lubricant in conventional aqueous pigment coating.

Calcium sulphate

This material ($CaSO_4$ in its anhydrous form) is present in the papermaking system from three possible sources:

- ❑ permanent hardness in the fresh water
- ❑ calcium sulphate (gypsum) used as a coating pigment
- ❑ from the interaction between calcium carbonate filler and added alum or sulphuric acid.

Except where calcium sulphate pigment is being used, the concentration of calcium sulphate is usually well below its solubility limit, but precipitates have been observed on recycled machines running under acid conditions and with quite closed water systems. The solubility of calcium sulphate is about 2.1 g/l at 25^{o}C, but declines with increasing temperature to about 1.5 g/l at 50^{o}C.

Calendering

This is the process of contacting the paper with a roll in order to create a smoother paper surface and perhaps to improve the cross-direction caliper uniformity. It is usually performed on-machine on the dried paper web although, because the web moisture has a profound effect on web compressibility, a controlled amount of water may be added to the web prior to calendering via water boxes or steam/mist showers. Calendering is carried out in a calender stack where the web passes through various nips between rolls of the same or different hardnesses. Supercalendering involves a combination of hard and soft rolls in the same nip. In most cases, calendering is thus a purely physical process, but the water boxes can sometimes be used for adding certain chemicals to the finished paper surface (eg sizes).

Caliper

This is the term for the thickness of papers, usually measured in microns or mm and is used in the calculation of sheet density (=grammage/caliper). Caliper may be used to distinguish between products labelled as papers or as boards. There is no universally-accepted demarcation line although a caliper of 0.3 mm is sometimes used. Caliper is particularly important for products where stiffness is a key property.

Canadian Standard Freeness

This is the name given to one of the two standard tests (the other being Schopper-Riegler) carried out on pulps to measure their drainage characteristics (freeness or wetness) and is used as an indicator of the progress of the pulp refining process. It is usually abbreviated CSF and has the units of volume (ml).

Carbohydrate

This is a generic term for compounds of carbon, hydrogen and oxygen which have the general formula $C_x(H_2O)_y$ (but not all chemicals having a formula that can be written in this form are carbohydrates, eg acetic acid where x=y=2). Their chemical name (at least for the simpler ones) usually ends in -ose and they are divided into two broad categories - the sugars and the polysaccharides. Soluble carbohydrates are often analysed in papermaking stock or water samples by simple colorimetric methods such as the reaction with phenol in the presence of concentrated sulphuric acid.

Carbon

This is the central element in organic chemistry and features in many of the materials used in papermaking. Carbon is the first element in Group 14 of the Periodic Table and the mass of its main isotope (^{12}C) defines the atomic mass unit or Dalton. Elemental carbon is used as a black pigment.

Carbonate

This divalent anion (CO_3^{2-}) is rarely encountered in the dissolved state at the wet end of paper machines as the pK value for the following reaction is too high (pK = 10 at 25°C).

$$HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$$

This means that very little dissolved carbonate will be present below pH 8.5, the upper pH limit for most paper machines. Carbonate is commonly present at the wet end of some paper machines in the particulate phase in the form of calcium carbonate. Any dissolution of calcium carbonate through interaction with acidity yields a mixture of bicarbonate and carbon dioxide. Sodium carbonate is sometimes added to the wet end to boost the alkalinity and give better on-machine sizing when AKD is used.

Carbon dioxide

Carbon dioxide (CO_2) is a sparingly-soluble, colourless gas, which is very important environmentally due to its involvement in global warming. The levels of CO_2 introduced into papermaking water systems are derived from three sources:

- ☐ the atmosphere, where the current concentration is about 370 ppm by volume (ppmv)
- ☐ the dissolution of calcium carbonates under acidic conditions
- ☐ the activity of micro-organisms.

Carbon dioxide plays a key role in the various equilibria that determine the balance of anions in the following series of reactions:

$$CO_2\,(g) \leftrightarrow CO_2\,(aq) + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$$

In accordance with Henry's Law, $[CO_2\,(aq)] + [H_2CO_3] = p_{CO2}/K_H$ where $pK_H = 1.5$ at 25°C

The equilibrium dissolved CO_2 concentration with atmospheric CO_2 is about 0.5 mg/l at 25°C, but decreases to about 0.3 mg/l at 50°C. The pH of deionised water in equilibrium with atmospheric CO_2 is about 6 at 25°C. Carbon dioxide is thus a sparingly soluble gas, but much higher concentrations can be dissolved in the form of bicarbonates and carbonates through the interaction with alkaline substances, which drives the above reactions to the right.

However, It is the local partial pressure of CO_2 that determines the equilibrium CO_2 concentration and this may be much higher (eg within an attached microbial slime deposit or near to a dissolving calcium carbonate particle) than in the external atmosphere. It is worth noting that, in producing a dissolved calcium level of 100 mg/l through dissolution of calcium carbonate, a similar concentration of CO_2 is released into the liquid phase. The resulting micro-bubbles of super-saturated carbon dioxide form larger bubbles as they attempt to reach the air surface and, during this process, become part of the entrained gas fraction.

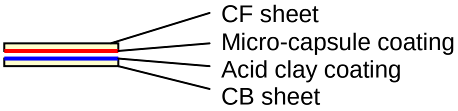
The kinetics of the absorption and release of CO_2 are not as fast as other reactions in the bicarbonate/carbonate equilibria and water systems are often super-saturated with respect to CO_2 due to poor mixing. When bicarbonates are present in the water entering the drying section with the paper sheet, the pH of the liquid phase will increase as the temperature of the sheet rises and CO_2 is expelled. This increased pH in the drying sheet may be an important factor in the curing of AKD sizes, where extra alkalinity in the form of bicarbonate or carbonate is sometimes added at the wet end.

Carbonless-copy paper

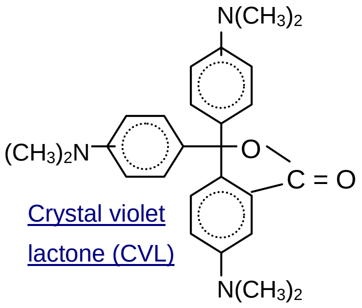
This is a speciality wood-free coated paper where two forms of coating are applied on opposite sides:

- the coated front (CF) sheet, which contains colour-forming micro-capsules.
- the coated back (CB) layer, where the coating is an aqueous acid formulation containing a bentonite or hectorite clay.

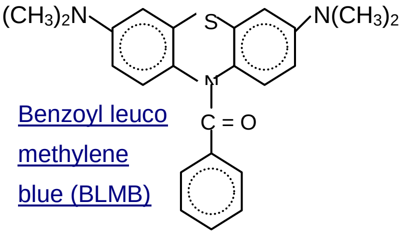
Intermediate sheets in a multi-copying set are coated on both sides (CFB sheets). The CF coating is an aqueous dispersion of the micro-capsules and graded starch granules, where the latter act as spacers (stilt) to keep the capsules apart. The capsule itself is a colloidal-sized particle (3-8 μm diameter) containing the colour-forming dye in an organic solvent. The actual capsule walls were originally made from natural polymers such as gelatin or gum arabic, but are now made largely of synthetic polymers such as polyamides or UF/MF resins.



Various dye precursors giving different colours may be used, two examples being shown at right. The CVL precursor is of the basic triphenylmethane dye type, which is not soluble in water. The lactone structure is broken in acid conditions and the changed conformation is a chromophor, but with poor light-fastness. The colourless BLMB pre-cursor also generates a chromophor under acid conditions, but this conversion also requires oxygen so the reaction rate is slow. These two compounds are complimentary and are usually both incorporated in the micro-capsule, the CVL giving an immediate colour whilst the colour from BLMB takes over when the first has faded.



Crystal violet lactone (CVL)



Benzoyl leuco methylene blue (BLMB)

The organic solvents have to possess a range of suitable characteristics such as being colourless and having a high boiling point in order not to increase the vapour pressure inside the capsule during drying as this would cause premature rupture. Suitable solvents are the alkylated biphenyls, alklyated naphthalenes (such as di-isopropylnaphthalene), chlorinated paraffins and some vegetable oils. Polychlorinated biphenyls were used for this application until the early 1970s. The mechanism of the copying action is that mechanical action on the CF sheet causes the capsules to break open and the initially colourless dye reacts with acidity in the CF coating to form the coloured image.

Carbonyl

This is a common functional group (C = O) in organic chemicals such as aldehydes, ketones, lactones, and carboxylic acids.

Carboxylic acids

These are organic compounds containing the -COOH group, which is present in many substances in papermaking:

- resin acids in the extractives fraction of virgin pulps
- fatty acids from various sources
- volatile organic acids (such as acetic acid) generated by anaerobic microbial activity
- glucuronic acid derivatives in hemi-celluloses
- pectin substances in virgin pulps
- oxalates present in some pulps
- rosin compounds used for sizing
- in the form of the acid anhydride in ASA size
- in the form of a keto-acid when AKD hydrolyses
- carboxymethylcellulose (CMC) additives
- anionic polyacrylamides used as retention aids
- polyacrylate dispersants used with fillers/pigments in slurry form
- polyvinyl acetate binders used in coating
- adipic acid used to make PAE resins and sometimes used with ASA size
- proteins that also have some basic properties
- alginates used in some coating formulations.

The simple ionisation reaction to form the carboxylate ion plays an important role in the functionality of many carboxyl-containing chemicals in papermaking.

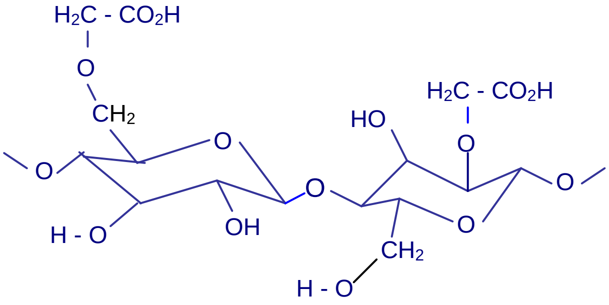
$$-COOH \leftrightarrow -COO^- + H^+$$

As the carboxyl group is usually only weakly acidic (pK value about 5), it typically ionises in the pH range 3-7, thus increasing the anionicity of the carboxyl-containing substance. This may be essential for the functionality of some additives (such as rosin and polyacrylates), but for other compounds (such as the resins acids which cause pitch and pectins which, when dissolved, contribute to anionic trash), it is the ionisation that causes the problems. The carboxyl content or anionicity of these materials can be measured by some form of charge titration.

There are many examples of such ionisation effects In this document - here for the effect of pH on the charge of a bleached Kraft pulp, here for the relationship between pulp zeta potential and anionic (carboxyl) group content and here for the effect of pH on the charge of pitch.

Carboxymethylcellulose (CMC)

This is a water-soluble derivative of cellulose used for range of applications in papermaking, but CMC is mainly added to the paper surface rather than at the wet end. It is made by the reaction between alkaline cellulose and chloroacetic acid, in which some of the cellulose hydroxyl groups are converted to carboxymethyl groups as shown at right. This depiction of the molecule shows the most common substitution at the 2 and 6 positions on the glucose unit. The polymer is usually produced as the sodium salt in a number of grades of varying molecular weight and degree of substitution (DS).



As the degree of substitution increases, the CMC becomes more hydrophilic and water-soluble. The normal degree of substitution is 0.2-0.3, so that there is on average one carboxymethyl group associated with every 1-2 glucose units, giving an anionic charge density of 1.8-2.5 meq/g. The anionicity of CMC ensures that the polymers adopt an extended conformation in solution at low concentrations, but they do become more coiled at higher concentrations, ultimately forming a gel. The degree of substitution influences the rheological properties of CMC solutions, which are thixotropic at lower DS levels and pseudoplastic at higher DS. CMC is produced in solution and powder form, the latter being soluble in cold water, but dissolution is more rapid in warm water (up to 50°C). CMC solutions are quite stable in terms of microbial degradation as CMC is poorly biodegradable.

CMC is used at the wet end of the paper machine, one of its most significant applications being to improve the performance (retention) of PAE wet strength resins. It can also be used as a dry strength additive at the wet end, usually in combination with another additive such as cationic starch. Because of its anionic character, CMC has also been used as a so-called formation aid to reduce fibre flocculation (see example here). Other wet end applications are to reduce linting and enhance porosity in wood-containing papers. Due to its good film-forming ability, CMC is used at the size press in combination with starch to enhance surface strength, water retention and optimum performance of fluorescent brighteners.

In coating applications, CMC is classified as a co-binder, but it also functions as a rheology modifier and water retention agent. It is most commonly used as a co-binder with latices, where it provides the viscosity and water retention otherwise lacking. CMC has a greater interaction with clay pigments than with calcium carbonates, particularly at high shear, so lower molecular weight CMC grades tend to be used with clays. As at the size press, CMC is particularly valuable in coatings through its ability to act as a good carrier for fluorescent brighteners.

Casein

This is a protein (in fact a phospho-protein) derived from milk, which contains both hydrophilic and hydrophobic amino-acids. It is used as a dispersing agent to prepare stable, anionic rosin dispersions and has also been used as a coating binder.

Catalase

This enzyme breaks down hydrogen peroxide to water. It is not used positively in papermaking, but is present simply as a result of the growth of micro-organisms. Minimising catalase activity within deinking systems that use hydrogen peroxide for bleaching is important as bleaching efficiency is otherwise reduced significantly. It can be controlled by dosing of glutaraldehyde.

Cation

This is the term for any simple ion that possesses a positive charge, the most common in papermaking being calcium (Ca^{2+}) and sodium (Na^{+}). It can also be applied to polymers with positively-charged groups, but this is not common.

Cationic

This is the term used to describe a substance that has a positive charge. In papermaking, this covers simple cations and more complex cationic polymers. It should be emphasised that all such polymers are actually neutral as supplied, but the term "cationic" means that the polymer backbone contains a number of cationic groups, which is always due to the presence of an amine group. However, this cationic charge is always balanced by an identical anionic charge in the form of simple anions such as chloride.

Cationic demand

This is a type of charge demand in which anionic substances in the sample react with added cationic chemicals. The cationic demand is measured by titrating the sample against a standard cationic chemical, usually a cationic polymer. There are various forms of this titration, which are discussed further under charge titration. The cationic demand may be measured on the whole sample or a fractionated sample, most commonly one containing only soluble materials, ie after sample filtration or centrifugation. The most common measurement units are charge equivalents (eq) per litre of sample volume (best for filtered samples) or per g of particulate solids (best for just the particulate fraction by deducting the liquid phase demand from the total demand).

The most common application of this measurement is to measure the cationic demand from anionic trash, ie of negatively-charged substances associated only with the liquid phase. Unless the level of these substances is being controlled via an online sensor such as a streaming current detector, their concentration on the paper machine is likely to be very variable (see this example for a newsprint machine).

Cationic dye

The charge on that part of the dye molecule that determines its colour properties is one way of classifying dyes. Cationic dyes are sub-divided into the traditional basic dyes and the cationic direct dyes.

Cationic polymer

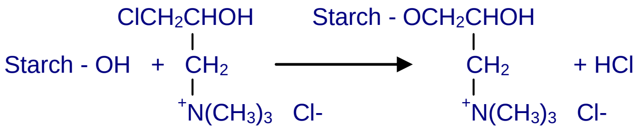
A cationic polymer is one with a number of positive charges on the polymer backbone, but with a balancing number of charges in the form of a simple anion such as chloride (Cl^-) associated with it. There are an enormous number of cationic polymers used in papermaking, the reason being the anionic charge of most particulate substances. A cationic charge thus provides an excellent driving force for that substance to be adsorbed on the particulate surface and thus retained in the paper. All cationic polymers possess a cationic charge due to the presence of the nitrogen atom in amine groups, which may be tertiary (attached to three carbon atoms) or quaternary (attached to four carbon atoms). The latter are preferable as they retain their cationic charge at all pH levels.

Cationic polymers cover a range of key papermaking functions:

- ☐ retention and drainage aids such as polydadmacs, polyamines, polyethyleneimines, polyvinylamines and the cationic form of polyacrylamides
- ☐ dry strength aids such as cationic starches and the cationic form of polyacrylamides
- ☐ wet strength aids such as polyamide-epichlorhydrin resins.

Cationic starch

Cationic starch is the most common, but not the only, starch type used at the wet end and it can also be used at the size press, but not usually for coating. As a dry strength additive, it is mainly used at the wet end where improved body strength is required in the paper, ie with papers using filler and recycled pulps or where pulp refining is undesirable, eg tissue grades. It is used at the wet end because of its superior adsorption characteristics over other starch types, which is also the main reason why it is sometimes used at the size press. Cationic starch is also used to emulsify some sizing agents (AKD and ASA) and its presence is often harnessed with some retention aid systems, eg with colloidal silica.



$$\text{Starch - OH} + \underset{{}^{+}N(CH_3)_3\ \ Cl-}{\overset{ClCH_2CHOH}{\overset{|}{CH_2}\underset{|}{}}} \longrightarrow \underset{{}^{+}N(CH_3)_3\ \ Cl-}{\overset{\text{Starch - }OCH_2CHOH}{\overset{|}{CH_2}\underset{|}{}}} + HCl$$

Commercial cationic starches are made by reacting a starch suspension with a suitable reagent such as chloro-hydroxy-propyl-trimethyl-ammonium chloride (CHPT) as shown at right below. However, some CHPT grades contain chlorinated contaminants such as dichloropropanol and epichlorhydrin, which is relevant if the paper may come into contact with foodstuffs. Using purer grades of CHPT, the level of such contaminants in the starch can be reduced to below the limits of detection and, at the same time, the starch is itself of better quality through eliminating side reactions between these contaminants and the starch.

Cationic starches are thus a type of etherified starch with the reaction mainly taking place at carbon 2 on the glucose unit. In the case illustrated above, the nitrogen responsible for the cationic charge is quaternary, but some cationic starches are produced utilising similar reagents, but with tertiary nitrogens. The latter do not maintain their cationic character under all conditions, as shown here in relation to the effect of pH. When the above reaction is applied to potato starches, the resulting product is more precisely an amphoteric starch due to the natural anionic phosphate groups already present.

The degree of starch cationicity is an important characteristic in relation to both the price and wet end performance of the starch. As the cationising agents are expensive weight-for-weight compared to native starch, the price of the cationised product increases significantly with cationic charge density. In order to improve the economics of cationic starch, attempts have been made to cationise raw starch at the paper mill, usually as part of the starch cooking process, but this has never been that popular.

The cationicity of starches can be quantified in three ways:

- by the degree of substitution (DS) of the starch, which is the average number of hydroxyl groups on each glucose unit that have been converted to a cationic entity, the maximum DS being 3.
- by measuring its nitrogen content, commercial cationic starches often being quoted on this basis. The relationship between DS and N content depends on the molecular weight of the cationising agent and is not linear.
- by charge titration with a standard anionic polymer using either a colorimetric or SCD end-point, the units then being equivalents per unit mass.

The range of starch cationicities using these three parameters is shown in the table below.

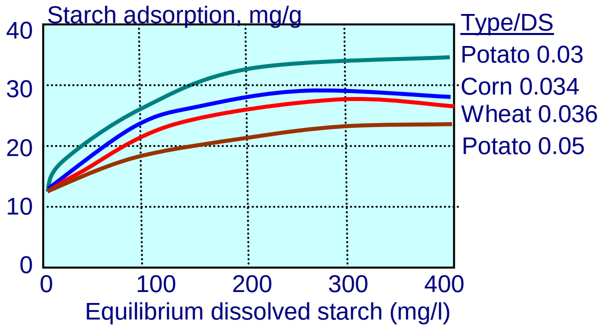
Cationicity	Degree of substitution	% nitrogen	Charge (meq/g)
Low	0.02	0.17	0.12
Medium	0.05	0.37	0.26
High	0.1	0.8	0.57
Super-high	0.2-0.3	1.5-2.2	1.1-1.6

Commercial cationic starches stop far short of the maximum cationicity and are usually in the range DS 0.03-0.3, ie between 1 and 10% of hydroxyls have been cationised or one in every 3-30 glucose units on average have a positive charge. Even with a low cationicity of DS 0.03, each amylopectin molecule (assuming a molecular weight of 10M Daltons) would have around 2000 positive charges and each amylose molecule (assuming a molecular weight of 0.5M Daltons) would still have 100 positive charges. The “super-high” cationic starches are approaching the cationicity of some fully synthetic cationic polymers (polyacrylamides), but are used more for charge neutralisation than for sheet strengthening.

All wet end additives like cationic starch must be retained efficiently in order to be able to express their functionality in the product and this depends primarily on their ability to be adsorbed by the particulate matrix. Clear interpretation of starch adsorption data on pulps is complicated by the heterogeneity of starch in terms of the molecular weights of its two fractions and their consequent differing accessibility to internal and external regions of pulp surfaces.

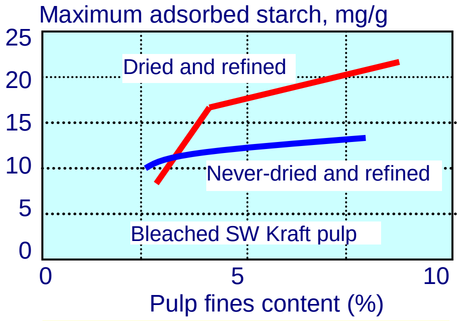
In any given papermaking system, the critical property determining the extent of cationic starch adsorption on the particulate matrix is the starch's cationicity. A typical plot of starch adsorption versus starch cationicity is shown here for a bleached Kraft pulp refined to 25^{o}SR. Maximum adsorption decreases with increased starch cationicity as expected for an electrostatic adsorption mechanism. Increasing the surface area for adsorption by pulp refining or adding filler enhances the adsorption maximum (as shown here), but starch retention increases only if the pulp fines/filler are themselves retained. This is illustrated here, where the starch retention declines because the pulp fines were not efficiently retained.

A variety of starch types are converted into cationic starches, the figure at right showing a comparison between potato, corn/maize and wheat starches (see also this figure for data on cationic tapioca starches). Taken at face value, the data indicates that, at comparable cationicities, the potato starch has the highest adsorption with the corn and wheat cationics being very similar. The amphoteric character of the potato starch may be an additional factor in its performance, although this experiment had no cationic substances present to help anchor the potato starch's anionic group.



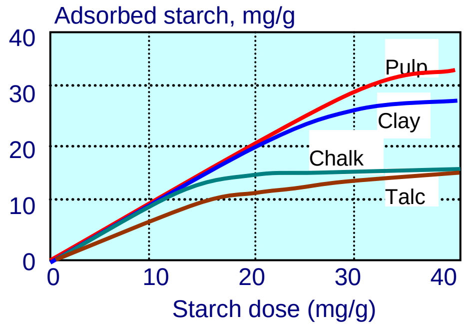
Source: Hedborg, Nordic Pulp Paper Research .J.,1993, 2, 258-263.

There have also been shown to be differences in the adsorption of cationic starch depending on a pulp's drying history. Never-dried bleached Kraft pulps (as used by integrated mills) have a lower adsorption potential than do the same pulps after drying (as used by non-integrated mills). The difference is due mainly to the fines from the dried pulp having a much greater adsorption potential (about 250 mg/g) than the fines from the never-dried pulp (about 150 mg/g) for cationic potato starches with DS 0.01-0.03. At higher DS values (0.05), the adsorptions are similar (about 70 mg/g fines) seemingly for steric reasons. Refining maintains the superior adsorption characteristics of the never-dried pulp and starch adsorption increases with fines content for both pulps, as shown at right for cationic starch with DS 0.03.



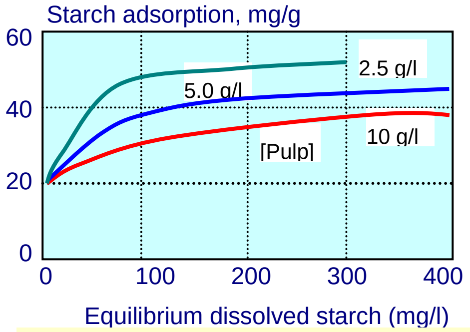
Source: Wagberg in Nordic Pulp Paper Research . J., 1993, 4, 399-404.

The presence of filler is quite common when cationic starch is being used as a dry strength agent so its effect on cationic starch adsorption is important. Fillers on their own show adsorption isotherms with a typical Langmuir pattern, as shown at left for a moderate cationic starch (DS = 0.03) on three fillers compared to a bleached Kraft pulp. Although the surface chemistry of the fillers is different, their maximum adsorptions are similar in relation to the surface area of the fillers (3-5 g starch/m^2). In practice, pulp and filler are often both present at the time of starch addition, so there will be some competitive adsorption between them, the outcome of which will be determined by many factors - mixing conditions, relative pulp/filler concentrations and surface chemistries. Differences in the latter may be negated by adsorption of pulp-derived organics (see examples and explanation here).



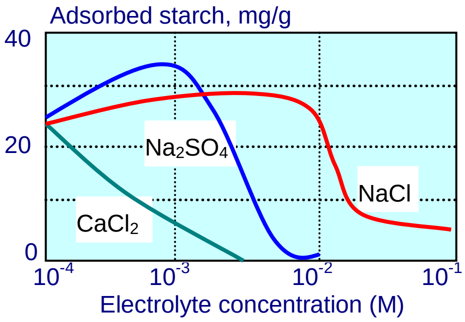
Source: Krogerus at Pira Conference "Recent developments in mineral use in papermaking", 1988.

Another wet end variable is the point of starch addition in terms of pulp (and filler) consistency. The Langmuir model of adsorption predicts that this has no influence, but this is true only when the adsorbent and adsorbate are homogeneous and mono-disperse, which is certainly not true for pulps and starches. The graph at right shows a typical set of data for a refined bleached softwood Kraft pulp, indicating better adsorption of this cationic potato starch at lower pulp consistencies. Similar patters have been shown for starch adsorption on fillers alone. This effect is usually attributed to the competitive adsorption between high and low molecular weight starch fractions depending on the surface-polymer ratio, whereby the low molecular weight fraction is adsorbed mainly at low surface-polymer ratios.



Source: Hedborg, Nordic Pulp Paper Research .J., 1993, 2, 258-263.

In addition to some of the furnish-related issues described above, there are three important wet end parameters that vary widely between machines and which can therefore influence cationic starch performance - temperature and the concentrations of electrolytes and anionic trash. The impact of temperature on the adsorption of a cationic starch was shown here, but it should be noted that this experiment was performed at round pH 4 when there will be a much reduced electrostatic driving force for adsorption due to the reduced charge on the pulp. At face value, the data shows an increasing adsorption with rising temperature, but this can only be explained by a decreased entropy on adsorption, which is unusual.

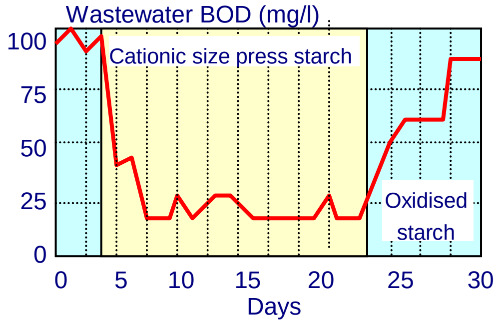


Source: Hedborg in Nordic Pulp Paper Research . J., 1993, 2, 258-263.

The effect of electrolytes on the adsorption of cationic starch is less uncertain, as shown at right, which is similar to the patterns for the adsorption of other cationic polymers (eg of polyacrylamides as shown here). The data here is for a refined bleached Kraft pulp at pH 8 with a cationic potato starch of DS = 0.05. The initial increase in adsorption for the increasing concentration of the sodium salts is attributed to shrinkage of the starch molecules due to decreased electrostatic repulsion between its cationic groups and greater accessibility to internal pulp surfaces. The higher electrolyte concentrations shield the attraction between the starch and anionic pulp surface so adsorption declines. For the calcium salt, there is competition with the cationic starch for the adsorption sites on the pulp, such that, at a calcium concentration of only about 100 mg/l, there is no starch adsorption. The latter is a very important effect in paper machine systems as dissolved calcium levels can easily exceed this level. For this reason, anionic starches may be more effective than cationic starches when there are high dissolved calcium levels.

In the above examples of cationic starch performance, the cationicity of the starch is no higher than a DS of 0.05, which was considered a high level until about the early 1990s. Since then, the upper limit for "normal" cationic starches (ie those used primarily for strength improvement at the wet end) has increased to around DS 0.1 in order to cope with more difficult wet end conditions on some paper machines, ie higher levels of electrolytes and anionic trash (see this example for performance of cationic starches with different DS on a deinked furnish with colloidal silica). However, cationic starches with DS levels up to 0.3 ("super-cationic" starches) have been developed by one supplier (Raisio), but not as a dry strength agent. In view of their high cationic charge (around 1-1.5 meq/g), these starches are being used mainly for neutralising anionic trash.

Cationic starches may also be used at the size press. Initially, the reason for this was due to their excellent adsorption properties, but, in this case, in relation to the ability of such starches to be retained with the particulate matrix when size press-treated broke is recycled. Data on the proportion retained in an adsorbed form at the wet end gives a figure of 10-30% for the normal range of non-cationic size press starches, but this rises to about 80-90% for cationic starch size press starches. Many applications of cationic starch at the size press have been driven by environmental factors related to lower wastewater BOD/COD loads, an example of which is shown in the figure below at right.



Source: Gl;ittenberg, D Paper ja Puu, 1997 79 4 240-243

Despite cationic starches having been shown to be technically more effective on a weight basis than some conventional size press starches and to give certain benefits (eg improved ink hold-out), cost effectiveness remains the big question for using cationic starches at the size press. However, there are several ways of justifying this through the savings in different aspects of wet end operation:

- lower microbiological control costs and fewer system cleans from the lower concentrations of dissolved starch
- better drainage and water removal
- reduced anionic trash if the cationic starch is replacing an anionic (eg oxidised) starch
- external savings from the lower BOD loads requiring treatment.

On machines using fillers, it is also possible to make use of the higher starch content in the base paper to use more filler or less fibre and get better retentions. These calculations can only be done on a case-by-case basis, but it is likely that a good justification could be made for many fine paper grades. The situation for the other grade which is a substantial user of size press starch (packagings) is less clear, particularly on recycled grades, where the wet end (and wastewater) chemistry is more affected by the incoming furnish than by the machine broke.

Cationic starches are not commonly used as coating binders due to their interaction with the negatively-charged pigments (particularly clays), which can generate unacceptably high viscosities under low- and high-shear conditions.

Caustic soda

This is an alternative name for sodium hydroxide.

Cellobiose

This is a disaccharide formed between two β-1,4-linked glucose units, which is the type of bond present in cellulose.

Cellulases

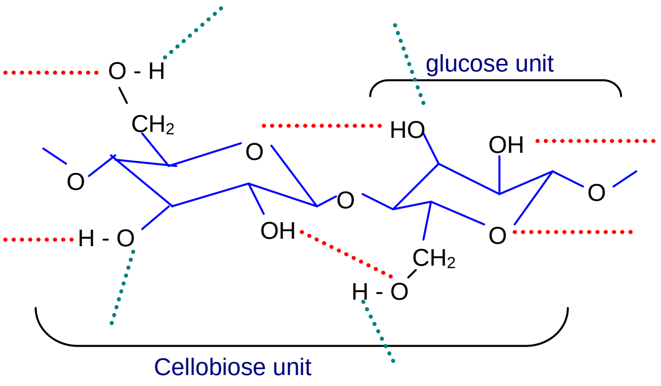
This is a generic name for a number of enzymes that catalyse the breakdown of cellulose molecules:

- endocellulases that break β-1,4 links at random in the amorphous regions of the cellulose
- exocellulases (such as cellobiohydrolases) that remove cellobiose units sequentially from the non-reducing end of the cellulose, even in crystalline regions
- cellobiase (also called β-D-glucosidase) that splits cellobiose into molecules of glucose.

Cellulase activity is more prevalent in fungi than bacteria. Extracted cellulases have been developed to aid ink removal in deinking systems and for improving drainage in papermaking.

Cellulose

This is sometimes referred to as α-cellulose, which is defined as that part of cellulosic material which is not soluble in 17.5% NaOH solution (in contrast to the β- and γ-celluloses present as hemi-celluloses). Cellulose is the most important component of papermaking pulps as it is the material which gives structure to the fibres and to individual fibrils. It is a linear polymer of β-1,4-linked glucose units with the structure of each repeating unit as shown at right. The length of each cellobiose unit is about 1 nm. Cellulose has a degree of polymerisation (DP) of 3,000-15,000 depending on its source, corresponding to a molecular weight of 0.5-3M Daltons. The chains in wood cellulose (DP about 10,000) are shorter than in some non-wood fibres such as flax and cotton (DP about 15,000).



Because of the β-1,4-glucosidic linkage, each glucose unit is effectively at an angle of 180° to the ones either side, so the cellulose molecule is like a twisted ribbon. The linear conformation of the cellulose chain is reinforced by intra-molecular hydrogen bonds between adjacent glucose units (as shown by the red-dotted lines above), which are parallel to the glucosidic link. Adjacent cellulose molecules are held together by further hydrogen bonds (as shown by the green-dotted lines above) to form elementary or micro-fibrils. This is the conformation in native cellulose (sometimes referred to as cellulose I), but it may be different for other forms (eg artificial celluloses such as celluloses II-IV).

Within the fibrils, the cellulose molecules take up different orientations to the fibre axis within each part of the cell wall and have their greatest concentration in the S2 layer. The conformation of the cellulose chains is sometimes ordered (in crystalline regions) and sometimes disordered (in amorphous regions) with a gradual, rather than instantaneous, change between the two. The content of cellulose in a crystalline form varies in the range 50-90% depending on fibre source, being highest in non-wood fibres like cotton. As a homogeneous polymer of glucose units, natural cellulose does not contain any groups that are charged at papermaking pH levels although it is thought that some might be introduced during pulping and bleaching. Cellulose can be converted to water-soluble derivatives, a good example being carboxymethylcellulose (CMC), which is itself used in papermaking.

Due to its insolubility, cellulose displays no reaction chemistry in papermaking other than its interaction with water via extensive hydrogen bonding. This is very important to the ultimate strength of the papermaking fibres and is discussed further under swelling.

CFU

This is an abbreviation for colony-forming units, which define the number of bacteria in a sample.

Chalk

This is one of the several different natural forms of calcium carbonate, the mineral used as a wet end filler or paper coating pigment. Chalk is a soft form of calcium carbonate consisting predominantly of the shells of sea animals (foraminifera).

Charge

The fundamental unit of charge is the Coulomb, which is the charge when a current of 1 ampere (amp) flows for 1 second. The charge on the electron itself is 1.6 x 10^{-19} Coulombs and each charge equivalent (abbreviated eq, the charge from 1 mole of electrons) is 96,490 Coulombs or one Faraday.

The term "charge measurement" in papermaking is used in a restricted sense and not in the sense of measuring all charged species in the system (see charge interactions). For example, charged materials such as simple ions are not included in "charge" measurement, but, as part of the electrolyte fraction, they can be quantified separately in the measurement of conductivity. Two different sets of charged materials can be quantified in what is referred to as "charge measurement":

- charges associated with particulate solids

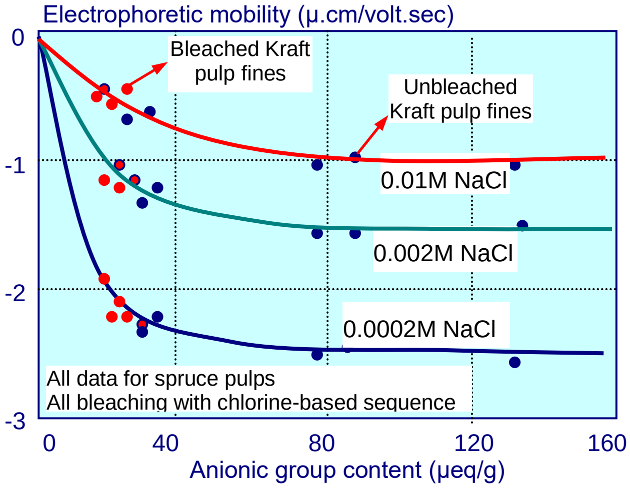
  These charges are measured either by an electrokinetic method as a potential (usually the zeta potential in millivolts) or by a direct titration method with an oppositely-charged species, in which case the result is expressed as charge equivalents (meq or μeq) per unit mass of solid.

- charges in the liquid phase

  These charges can only be measured by a titration technique with an oppositely-charged species and are expressed as charge equivalents (meq or μeq) per unit volume (usually litre) of solution.

When the charge is measured by a charge titration, these charge values are sometimes referred to as a charge demand, which may be anionic or, more commonly, cationic.

It should be noted that charge or charge demand (in meq/g) is an extensive property of the system, whilst potential is an intensive property. A suspension containing 1 g/l of particles has the same measured potential as a suspension containing 10 g/l of particles, but the titrated charge will obviously be different by a factor of about 10. It would be expected that the particle potential increases with the content of charged substances and this is shown in the figure at right (which uses a titration with a cationic dye to measure the anionic group content of some unbleached and some bleached Kraft pulps). The shape of the curve, which asymptotes to the x-axis, is consistent with the theoretical relationship between the zeta potential (or electrophoretic mobility) and surface charge density developed from the Gouy-Chapman treatment of the electrical double layer.



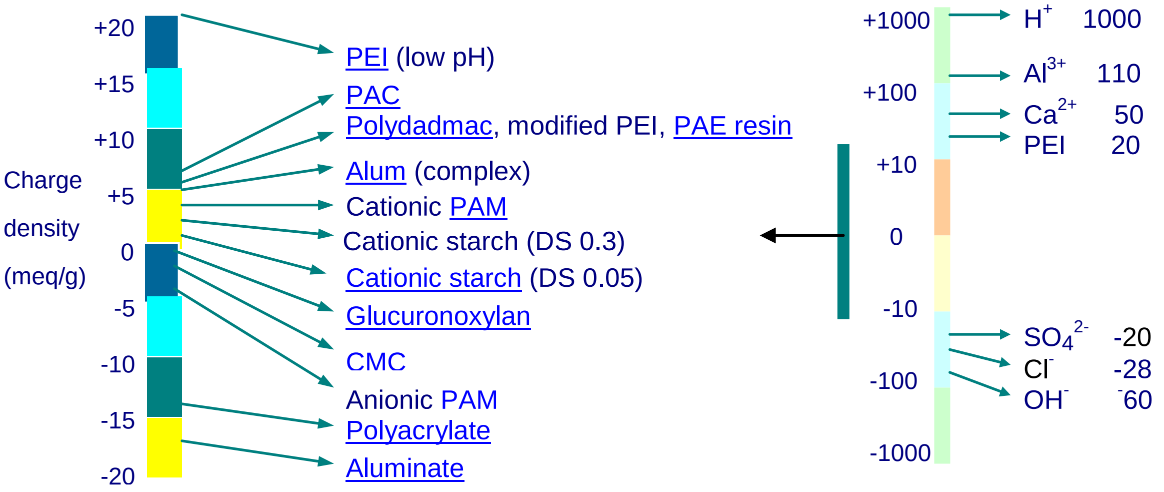
Source: Goulet and Stratton, Nordic Pulp and Paper J., 1990, 3, 118-122.

Charge demand

This term refers to the technique of carrying out a titration of one type of charge (usually negative ones from anionic species such as anionic trash) within the papermaking sample against a standardised solution of opposite charge (usually positive ones from cationic species). When the standard titrant is cationic, the result is the sample's cationic demand. The anionic demand can also be measured by titration with an anionic polymer, but this is not very common as this demand is usually very small. The analytical techniques are discussed further under charge titration.

Charge density

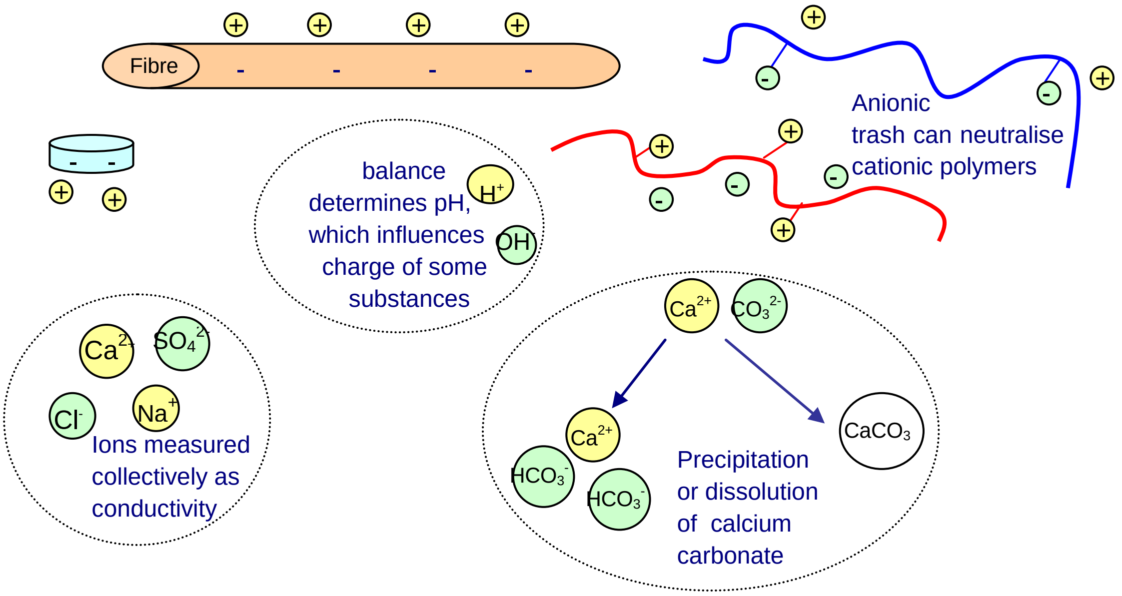
This term is most commonly applied to charged polymers, but it can also be applied to ions for comparative purposes. The most convenient unit is meq/g dry material as illustrated at right for various papermaking substances.



Charge interactions

The charged species in papermaking waters range from simple ions to complex polymers, all of which can interact with one another in different ways (see figure above):

- reactions between cations and anions which may lead to precipitation such as that of calcium carbonate and calcium sulphate
- the balance between protons and hydroxyl ions determines the system pH, which has obvious implications in terms of corrosion of construction materials and more subtle effects on the charge of other materials and hence on their interactions.
- repulsion between the various particulate solids due to their normal anionic character. Mutual aggregation can occur when the anionic surface charge is reduced by cationic additives or by high electrolyte levels, but the strength of the aggregates thus formed is quite weak and easily broken by shear forces unless some inter-particle bridging is involved.
- between particles and oppositely-charged dissolved solids. This can take the form of a stoichiometric exchange of ions between the surface and the liquid phase or the adsorption of polymers, which may not necessarily be charge-stoichiometric. Adsorption is a very important process in papermaking as it is a crucial step in the retention of many (usually cationic) paper additives and in the functioning of polymeric retention and drainage aids.
- between oppositely-charged dissolved polymers, notably between added cationic additives and anionic substances originally present largely in pulps (anionic trash).



Charge neutralisation

This is a very general term that might be used in papermaking in relation to the complete or partial neutralisation of charges (usually negative ones) associated with either particulate substances (pulp, filler) or with dissolved substances (typically the polymers responsible for anionic trash). Clearly, charge neutralisation of this type can only be brought about by cationic additives such as PAC and cationic polymers. Occasionally, the term might be used in the opposite sense, for example where anionic substances (eg CMC) are added to partially neutralise the cationicity of PAE wet strength resins. Charge neutralisation is also the basis for the various off-line or on-line techniques used to quantify such charges by some form of charge titration.

Charge titration

This term is used to describe the various analytical techniques for determining certain types of charged species in papermaking. Many types of ordinary titration are between oppositely-charged species (eg protons with hydroxyl ions in acid-base titrations), but they are not usually included within the meaning of this term as applied to papermaking systems. In most cases in papermaking, the titration is of an anionic charge in the sample (most commonly due to an anionic polymer) with some form of cationic chemical. The result is sometimes termed the sample's cationic demand.

There are different types of charge titration, which vary between one another in several key ways, all of which may influence the result:

❑ the nature of the sample

The titration may be carried out on the whole sample (particulate and dissolved solids) or just the dissolved solids (after filtration or centrifugation of the whole sample).

❑ the nature of the titration, there being two types:

- direct titration, where the sample is titrated against a cationic substance
- back-titration, where an excess of cationic substance is added to the sample and the excess is titrated against an anionic titrant.

One of the differences between these is the different kinetics between adding a cationic polymer to the sample slowly (as in the direct titration) and rapidly (as in the back titration). The direct titration is the most common approach.

- ❑ the nature of the added cationic species, which can be any of the following:
  - protons using a potentiometric or conductometric end-point determination
  - metal cations, usually using some form of colorimetric end-point to indicate excess cation
  - cationic dyes (eg methylene blue) using a direct colorimetric end-point involving the dye itself (see this example of charges on chemical pulps by this technique)
  - cationic polymers using either the classical colorimetric end-point associated with the colloid titration technique or the electrokinetic end-point based on a zero streaming current. This is sometimes referred to as a polyelectrolyte titration. The cationic polymers used are typically of moderate charge density (5-6 meq/g), but can differ markedly in their molecular weight (and hence in their size). This differing accessibility to pulp surfaces can be turned to an advantage by deliberately using polymers of differing molecular size to determine the total charge (using small 8k Dalton polymers such as Polybrene) and the external surface charge (using a larger 300K Dalton polymers such as a polydadmac). Examples of the differences in titrated charge for these two polymers on various pulps is given in this table. This use of polymers of defined molecular size is analogous to their use in the reverse solute exclusion technique for quantifying fibre swelling

It is also possible to measure the sample charge by chemical analysis, for example in the case of the most common carboxylic acid groups, by conversion to the methyl ester which is then measured by gas chromatography. This is useful as an independent cross-check, but is rarely done except in research studies.

It would not be too surprising if different results on the same sample were obtained between these techniques, there being two key sources of variability:

- ❑ the possible non-stoichiometry of the reactions due to steric constraints, notably with samples containing particulate solids, but also possible with samples containing only dissolved solids.
- ❑ the non-accessibility of the added cationic material to the site of the anionic charge, which is an issue only for charges associated with pulp surfaces, not with dissolved solids.

Both issues are most pertinent to the commonest type of titration (those conducted with polymers) as protons, metal cations and dyes are small enough to be able to access and react stoichiometrically with all anionic charges. As mentioned above, non-accessibility is mainly a problem for high molecular weight polymers on samples of low electrolyte content (when charged polymers have the most extended conformation) and non-stoichiometry is more of a problem on samples with high electrolyte levels (when the added polymer chains are quite coiled and the charges possibly "hidden").

The table directly below gives a very useful comparison of these techniques on various pulps (note that the pulps were thoroughly washed to remove dissolved substances prior to analysis). Without analysing the above data in minute detail, it is evident that there is both quite a wide spread in the results on the same pulps and also quite good agreement between certain methods (potentiometric, conductometric and dye adsorption). As the charge values from the polymer titration are generally higher than from the other techniques, this would seem to confirm that this low molecular weight polymer is small enough to access all the pulp charges. These higher values may result from continued polymer adsorption beyond the point of neutral charge. There are many other examples of charge titration data in this document, notably in the sections on bleached Kraft pulps, bleached mechanical pulps, ECF pulps, refining, TCF pulps, thermomechanical pulps and unbleached Kraft pulps.

PULP CHARGE CONTENT (μeq/g) BY DIFFERENT TECHNIQUES

Pulp	Conducto-Metric	Potentio-Metric	Cation (Zn) exchange	Dye (MB)	Polymer	
					0M NaCl	0.01M NaCl
UBK pine	124	95	98	115	95	152
TCF BK birch	66	87	56	68	102	82
ECF BK pine	40	38	37	37	58	43
ECF BK eucalypt	83	70	60	77	110	105
TMP spruce	87	85	65	92	106	89
Bleached TMP spruce	178	176	113	178	228	182
BCTMP spruce	187	187	160	188	260	201
Deinked office papers	64	70	8	63	87	95

Notes: Polymer titration with Polybrene using back-titration technique with KPVS and SCD end-point
Source: Fardim et al in Nordic Pulp Paper Research J., 2002, 17, 3, 346-351.

Chelant

This is a term which describes chemicals that can form strong complexes with certain cations and thus stabilise them in a water-soluble form. This may be useful in preventing cations from reacting with certain anions, which would otherwise result in a precipitate being formed. Examples of such chemicals are polyphosphates, EDTA and DTPA. The latter is quite commonly used in bleaching with oxygen and hydrogen peroxide in order to prevent catalytic decomposition from certain metal ions. Chelants are not that widely used in papermaking due to their efficacy being dependent on stoichiometric (high) doses (eg for preventing calcium carbonate precipitation from calcium bicarbonate), but they may be present in cleaning formulations to prevent precipitation reactions.

Chemical bonds

Reaction chemistry involves the formation of new chemical bonds, whereby the electrons in the various atoms or molecules present are re-arranged to yield a more stable (lower free energy) configuration. The number of bonds that any element can form is determined by its valency. There are five main types of chemical bond:

- ❑ ionic bonds as in electrolytes such as sodium chloride (Na^+Cl^-), in which the bonding electrons are transferred from one atom (in this case, sodium) to another (in this case, chlorine), the two ions being held together by the strong electrostatic attraction between them. In the solid state, this often leads to very ordered, crystalline structures.
- ❑ covalent bonds as in most organic compounds such as cellulose and starch, in which the bonding electrons are shared between both atoms due to an overlap of the electron orbitals. These bonds are usually written as a dash, as in a single carbon - carbon bond, C - C.
- ❑ co-ordinate bonds in which the bonding electrons are donated by only one of the bonding entities and then shared between them, eg in the complexes that aluminium ions form with water molecules and that chelants form with cations. This is usually considered as a special case of a covalent bond and is normally written as an arrow, as in $O \rightarrow Al$.
- ❑ metallic bonds might be considered a type of covalent bond in the sense that the valency electrons are not "owned" by one atom, but are readily exchanged in a virtual "sea of electrons". Metallic bonds have great strength, which increases with the number of valency electrons.
- ❑ hydrogen bonds, which are present when hydrogen is bonded to certain electrophilic elements and is very important in relation to the strength of all paper products and to the unique characteristics of water.

Chemical pulps

These pulps account for about 80% of total virgin pulp production. Chemical pulps could be classified into unbleached and bleached grades, but a better initial classification is in terms of the pulping chemistry:

- ❑ soda pulps, mainly produced from non-wood fibres such as straw
- ❑ sulphite pulps, which have declined enormously due to environmental problems in their production
- ❑ sulphate (Kraft) pulps, which are the predominant chemical (wood) pulp produced today.

Even though they can use quite high doses of chemicals, chemimechanical pulps are best classified as a special type of mechanical pulp as, other than the chemical pre-treatment stage, the process is the same as it would be for a normal mechanical pulp. Chemical pulps are used extensively in many paper grades, the main sub-division depending on their brightness:

- ❑ unbleached chemical pulps, notably unbleached Kraft pulps, which are used mainly in the production of packaging papers.
- ❑ bleached chemical pulps, notably bleached Kraft pulps, which are used in the production of many paper grades.

Chemical oxygen demand (COD)

This is a measurement most commonly applied to mill wastewaters, but it is also often used to measure the level of dissolved organics at the wet end. An alternative technique is dissolved organic carbon. COD is measured by refluxing the sample in the presence of potassium dichromate and 50% sulphuric acid at a temperature of 150^{o}C (the boiling point of the mixture) for 2 hours and then measuring the residual dichromate by titration or colorimetry. Under these conditions, most organics (including lignins and cellulose) are oxidised stoichiometrically to carbon dioxide and water. A small quantity of silver sulphate is incorporated into the digestion mixture as an oxidation catalyst and some chromium (III) sulphate to prevent interference from chlorides.

The standard COD apparatus is simply a round-bottomed flask, reflux condenser and heater, but is rather space-consuming when many analyses have to be carried out. It has been minituarised by many equipment suppliers in the form of a small electrically-heated digestion block with places for 10-20 digestion tubes. This makes a very compact, easily-transported system that occupies very little bench space. The standard digestion time of 2 hours can be reduced to about 30 minutes with little loss of recovery for most paper mill waters.

For a carbohydrate polymer like starch, the COD is about 1.2 times its mass. For wet end measurement, it is best applied to the dissolved solids fraction as measuring COD on the whole sample will also include the contribution from fibrous solids (which are best quantified separately as part of the particulate fraction). COD levels on the paper machine range from a few hundred to several 10,000 mg/l (absolute maximum about 40,000 mg/l) depending on pulp type, broke level and the degree of water closure. Examples of COD levels are shown here for a coated wood-free paper machine, here for a recycled wet strength towel machine, here for a multi-ply board machine, here for organics dissolution from various recovered papers, here for organics dissolution in bleaching a mechanical pulp and here for the levels during washing of a bleached mechanical pulp.

Chemimechanical pulps

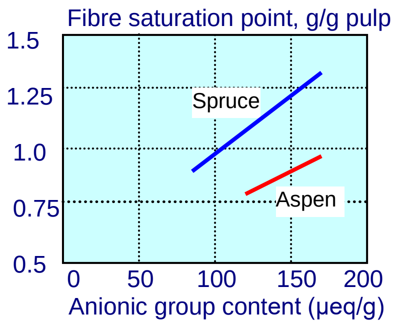
These variants of mechanical pulps were developed to combine the high yield of normal mechanical pulps with improved strength, but without sacrificing too much bulk or opacity. They are produced by chemical pre-treatment (impregnation) of the wood-chips, there being two distinct approaches:

- impregnation with sodium sulphite (1-5% on fibre) under slightly alkaline conditions with a low dose of caustic soda
- impregnation with hydrogen peroxide (about 4% on fibre) under stronger alkaline conditions, usually with the impregnation taking place over2/3 stages.

Impregnation is followed by normal mechanical pulping, but is more commonly used prior to refiner rather than groundwood pulping. Early CTMP plants were mainly applied to softwoods, but the current breakdown is about 50:50 between hardwoods and softwoods, largely due to new markets developed for the hardwood CTMPs. In contrast to the situation for normal mechanical pulp mills, many of the CTMP plants are not integrated, but are supplying market pulp to external customers. Frequently, such pulps are also bleached (usually with hydrogen peroxide) and can achieve brightness levels (80% ISO for softwood pulps and 85% ISO hardwood pulps such as aspen and eucalypt), which approach that of bleached chemical pulps. The numerous designations for these pulps can be confusing, but the most common are chemithermomechanical pulps (CTMPs) and bleached CTMP (BCTMP). The alkaline peroxide pulps are usually referred to as APPs.

As mentioned above, these pulps are not generally used in the traditional markets for mechanical pulps, but have developed uses in rather different grades as a replacement for bleached chemical pulps. These applications take advantage of their particular combination of qualities, the main outlets being:

- hardwood BCTMPs in printing/writing papers to replace bleached hardwood Kraft pulps at a level of 5-15% of the base paper in coated grades and 10-30% in uncoated papers
- softwood BCTMPs in tissue, where the combination of reasonable strength and high bulk/ absorbency are particularly valuable.

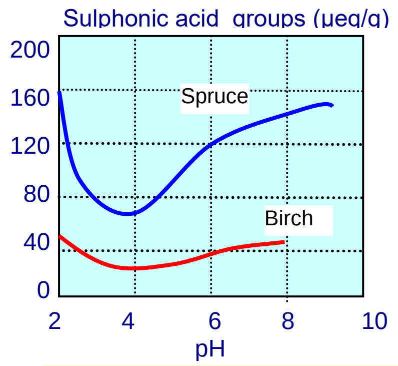


Source: Katz in Tappi J., 1981, 64, 7, 97.

The higher strength of chemimechanical pulps is a consequence of their enhanced swelling ability, one example of this being shown at left for pre-treatment with caustic soda (as in alkaline peroxide pulping). Under these non-oxidising conditions, the anionic group content increases solely as a result of alkaline hydrolysis of methyl esters of carboxyl groups. Swelling then increases due to the greater osmotic pressure across the fibre wall, but the swelling is not as great as in chemical pulps when compared at the same anionic group content - this due to the stiffening effect of the lignin that is still present.

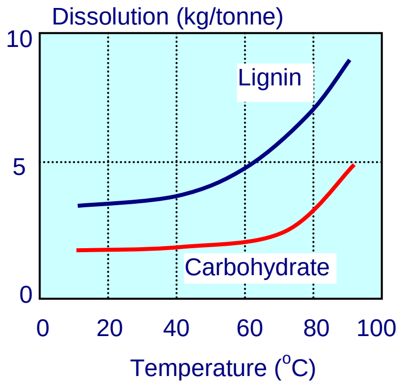
The yield of CTMP/BCTMP pulps can be as low as 85%, so management of the liquors containing the high levels of dissolved solids is much more important than in normal mechanical pulping processes. Some CTMP mills have developed fully-closed water systems, which have included the use of treatment stages (eg liquor evaporation) more commonly associated with chemical pulp mills. Irrespective of the precise yield, the high dissolved solids levels (plus the fact that many CTMP mills are not integrated so pulp drying is necessary) means that all mills of this type use some form of final washing to minimise the dissolved solids in the dried pulp. It has been found that one of the best techniques to minimise the pulp's dissolved solids is to pre-soak the bleached pulp in hot water (50°C) for 30-60 minutes followed by thickening to high (40-50%) consistency. Some CTMP manufacturers have managed to manipulate the fines content and charge characteristics of their pulps for different applications such as tissue.

In terms of wet end chemistry on the paper machine, the key issues for these pulps are the same as for mechanical pulps - fines content, pitch and the level of dissolved substances, but the latter is more critical because of the chemical changes that occur by virtue of the chemical pre-treatment. The fines content of chemimechanical pulps tends be lower (around 20% for softwoods) than that of normal mechanical pulps, but the content of anionic substances is increased. When mechanical pulps are pre-treated with sodium sulphite, some of the pulp lignin is sulphonated, which lowers its softening temperature.



Source: Sjostrom in Nordic Pulp Paper Research J., 1989, 2, 90-94..

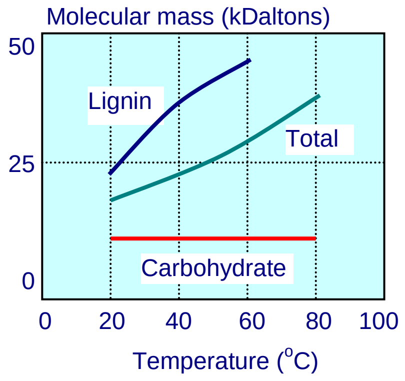
In the example at left, it is clear that the extent of sulphonation is greatest under acid or neutral/alkaline pH conditions and is greater with softwoods (spruce) than hardwoods (birch). In both cases, sulphonation is concentrated in the outer part of the cell wall. In contrast to the anionic hemi-celluloses, the sulphonate groups are fully ionised even under acidic conditions. As with ordinary mechanical pulps, peroxide bleaching of chemimechanical pulps also increases the content of anionic substances, in one case quoted the carboxyl content rising from about 100 μeq/g to 150-250 μeq/g. Bleached CTMPs thus have a very high content of anionic substances with a total (carboxyl + sulphonate) charge content of 200-300 μeq/g. In one case reported, the charge accessible to a low molecular weight polmer was only about 10% of the total charge. Charge data for a bleached CTMP in this table are consistent with the above values, indicating a total charge of around 200 μeq/g using various charge titration techniques.



92% yield chemithermomechanical pulp from mixed softwoods with 6 hour dissolution time

Reference: Willis and Goring, Tappi J., 1987, 70, 1, 105-106.

For mills using purchased chemimechanical pulps (the normal situation for these pulps), dissolution of organics depends on conditions within the paper machine system. This is illustrated in the figures here, the first of which (at right) shows increased dissolution of both lignins and carbohydrates at higher temperatures, particularly above 70°C. The greater fibre swelling and pore size at high temperatures allows larger molecular mass material to diffuse from the cell wall, but, as shown in the second figure at left, this is only important for the lignin fraction. A temperature rise due, for example, to increased water closure, would thus facilitate dissolution.



Chemistry

This is, of course, the subject of this document (or at least that tiny fraction relating to paper) and can be defined simply as the study of compounds and their interactions. It is an enormous subject, which is broken down into three principal branches:

- ❑ inorganic chemistry, which is the chemistry of the elements (see the Periodic Table) and their compounds, including that of elemental carbon, its oxides and metal carbonates
- ❑ organic chemistry, which is the chemistry of carbon compounds, excluding that relatively small part covered in inorganic chemistry
- ❑ physical chemistry, which is the study of the physical changes associated with chemical reactions and the dependence of physical properties on chemical composition.

It should be pointed out that chemical compounds (particularly organics) are often referred to both by their common names and their official names, the latter being defined by the International Union of Pure and Applied Chemistry (IUPAC).

The chemistry of paper can be broken down into the chemistry of raw materials, of the papermaking process, which is sub-divided into wet end chemistry and dry end chemistry and of the products themselves.

Chitosan

This is a derivative of the natural polymer, chitin, which is obtained from the shells of sea animals. Chitin is similar to cellulose in that it is a polymer of β-1,4-linked glucose units, but, in this case, the hydroxyl on carbon 2 in each glucose unit (see this picture) is replaced by an N-acetylamine group (CH_3CONH-). The name for this monomer unit is N-acetylglucosamine. Like cellulose, this material is insoluble in water, but it can be converted to the water-soluble chitosan by alkaline de-acetylation:

$$\text{Glucose - NHCOCH}_3 \rightarrow \text{Glucose - NH}_2$$

Commercial chitosan products vary in their degree of deactivation (and hence solubility) and molecular mass, these two characteristics being linked as the deacetylation reaction tends to depolymerise the chitin. The molecular mass of chitin is 1-3M Daltons, but that of chitosan is lower, typically 0.1-0.5M Daltons. Chitosan itself is still insoluble, but is converted to a soluble salt form by protonation of the amine under acid conditions, eg to form the hydrochloride (glucose - NH_3Cl).

Chitosan has been investigated for various applications in papermaking, but is still little used, partly due to its high cost compared to competitive materials. It can function as a wet end strength additive due to its ability to adsorb onto cellulose through its structural similarity and its cationic character under acid conditions. However, this can over-flocculate the pulp to the extent that the impaired paper formation can negate its strengthening effect. Chitosan can also be precipitated onto the pulp by raising the pH and this has been shown to introduce both dry and wet strength into the paper. Recent work using chitosan with AKD size under neutral/alkaline conditions has also shown its ability to boost the level of sizing, this being attributed to the deposition of cationic chitosan on the pulp. Surface application of chitosan has also been shown to give improvements in dry and wet strength.

Chloramines

These are formed when chlorine or sodium hypochlorite react with any ammonia present in the water. This reaction can take place during disinfection of fresh water or when free chlorine is present within the wet end, normally from the use of chlorine-release chemicals like the halogenated hydantoins. As the chlorine to ammonia dose increases, a series of increasingly chlorinated amines are formed (NH_2Cl, $NHCl_2$, NCl_3) until the "breakpoint" is achieved when all the ammonia is fully oxidised to nitrogen gas. The chloramines are much weaker disinfecting agents than chlorine, but are longer-acting. Similar reactions may take place when using ammonium bromide.

Chloride

This is a very common anion (Cl^-, molecular weight 35.5) and is the predominant ion in sea water. In papermaking, it arises from various sources:

- ❑ fresh water, particularly if brackish or saline
- ❑ as the product from reduction of chlorine and sodium hypochlorite
- ❑ the addition of poly-aluminium chloride
- ❑ as the counter-ion with most cationic polymers such as cationic starch and polyacrylamides
- ❑ residual chlorides in virgin or deinked pulps, notably those bleached with chlorine-containing compounds
- ❑ sodium chloride added at the size press.

As a very water-soluble ion with no tendency to form precipitates with cations or to adsorb on surfaces, the concentration of chloride at the wet end is dictated solely by its input load and the effect of the degree of water closure on the load coming from non-water sources (see these values for several machines with fully-closed water systems). Line A in this diagram could represent the change in chloride concentration with degree of water closure, chloride concentrations in most cases being no more than a few hundred mg/l. In addition to its contribution to overall conductivity, its presence is mainly important in relation to its potential corrosive action on metals. It can be analysed for by the classical titration with silver ions or by ion chromatography.

Chlorinated paraffins

These are organic liquids used as solvents for the colour-formers in the manufacture of some carbonless-copy papers. They are produced by chlorination of C_{10} - C_{17} paraffins and contain 30-70% chlorine.

Chlorine

This element belongs to the halogen group (17) and exists as a yellow-green diatomic gas (Cl_2) at ambient temperatures. It is a strong oxidising agent:

$$Cl_2 + 2e^- \rightarrow 2Cl^- \text{ where } E_H^o \text{ (redox potential) } = +1.4 \text{ volts at } 25^oC$$

It is manufactured from sodium chloride by various electrochemical methods based on the following reaction:

$$2NaCl + 2H_2O \rightarrow Cl_2 + 2NaOH + H_2$$

Chlorine has been used extensively in the bleaching of chemical pulps, but this has declined enormously in many countries since the late 1980s due to concerns about the production of chlorinated organic by-products such as chlorinated phenolics and dioxins. The role of chlorine in pulp bleaching has been taken over by chlorine dioxide for the production of ECF pulps and by a range of non-chlorinated oxidants for the production of TCF pulps. This pressure on the use of chlorine has also extended to its much smaller use in the bleaching of deinked pulps and of mill broke.

It can be used in a gaseous form in papermaking for fresh water disinfection, but this is also declining due to safety concerns about gas storage and handling. However, it is still used for various applications in papermaking in two other forms:

- ❑ in solution form as sodium hypochlorite for water disinfection, for broke bleaching and for disintegration of wet strengthened broke
- ❑ as an organic chlorine (and bromine) release compound such as BCDMH.

Chlorine is also present in many papermaking raw materials as the chloride ion or as organo-chlorine compounds. It is also used combined with oxygen as chlorine dioxide.

Chlorine dioxide

This is a strong oxidising gas widely-used for the bleaching of chemical pulps, particularly since the move away from chlorine bleaching. It is the main oxidant used to remove residual lignin in ECF pulps. Because of its unusual electronic configuration with an unpaired electron, it is a powerful oxidising agent under acid conditions:

$$ClO_2 + 4H^+ + 5e^- \rightarrow Cl^- + 2H_2O \text{ where } E_H{}^o \text{ (redox potential)} = +1.6 \text{ volts at } 25^oC$$

Because of its instability, it is always produced on site and there are many reaction schemes for this based on either sodium chlorite (sometimes referred to as stabilised ClO_2) or sodium chlorate as the starting materials. For the smaller production rates associated with its use as a biocide (rather than for full-scale pup bleaching), the most common production route is from sodium chlorite using chlorine gas or more commonly using sodium hypochlorite and acid:

$$2NaClO_2 + NaOCl + 2HCl \rightarrow 2ClO_2 + 3NaCl + H_2O$$

Apart from its extensive use in pulp bleaching, it is not widely used for bleaching of deinked pulps or in papermaking. However, it has been shown to be effective at destroying the fluorescence from brightening agents at neutral/alkaline pH at low doses (1-5 kg/tonne pulp). It is used by some mills for fresh water disinfection, where it has the advantage over chlorine/hypochlorite of being unaffected by pH and by the presence of organics or ammonia. Because of its non-reactivity towards carbohydrates, chlorine dioxide can also be used as an on-machine biocide and there is some evidence that, for paper machines using ASA sizing, it can help to detackify ASA deposits.

Chloroform

This chemical ($CHCl_3$) is not used as such in papermaking, but it is generated when chemical pulps are bleached with sodium hypochlorite. It would not be present in dried pulps due to its volatility.

CHPT

This is an abbreviation for chloro-hydroxy-propyl-trimethyl-ammonium chloride, one of the reagents used to introduce a cationic charge into starches. CHPT may contain other chlorinated organic compounds (such as dichloropropanol) depending on its purity.

Chromium compounds

Chromium is a transition metal and heads Group 6 of the Periodic Table. It is most ubiquitous in papermaking systems in a metallic form as a key component of stainless steel, which is essential, at least in some machine systems, to combat corrosion. However, chromium compounds have found some specialised applications in papermaking, the two main ones being:

- fluoride complexes of chromium, which have been used for making paper resistant to greases and oils by surface application
- chromium (III) complexes with fatty acids (eg myristic and stearic acids), which have been used to make paper hydrophobic, notably for release papers. The mechanism of their action is rather similar to alum/rosin sizing, where the chromium anchors the fatty acid to the paper surface with the optimum orientation.

Chromogen

This is the term for that part of a dye molecule that makes it adsorb light in the visible region of the electro-magnetic spectrum.

Chromophores

These are functional groups that are incorporated in a dye molecule to shift light absorption to longer wavelengths (called a bathochromic shift) and give a greater depth (blueness) to the expressed colour. Chromophores are mainly electron-accepting (electrophilic) groups such as the azo group, the keto group and the ethene or ethylene group. However, electron-donating (nucleophilic) groups such as hydroxyl and amino groups that lower the absorption wavelength (called a hypsochromic shift) may also be incorporated into the molecule. Nucleophilic groups also function as auxochromes.

CIE

This abbreviation stands for the Commission Internationale d'Eclairage (International Commission on Illumination), whose work is relevant to measurement of the optical properties of paper, notably whiteness, brightness and colour.

Clay

This is the name for a range of minerals that are composed of alternating layers of silica with other metal oxides/hydroxides. Their most characteristic property is a high degree of anisometry leading to a flat, platy structure. They are usually sub-divided into 4 sub-groups:

- the kaolinite group, which are alumino-silicates and include the important kaolin clays used as papermaking fillers and pigments
- the montmorillinite/smectite group, which includes other metal oxides/hydroxides in addition to alumina (eg magnesium) and contains three papermaking materials - talc, bentonite and hectorite
- the illite group, which contains no papermaking materials
- the chlorite group, which also contains no papermaking materials.

Closing up

This is a generic term that is widely-used in papermaking to denote the use of less fresh water on the paper machine, which results in a smaller flow of wastewater. The total use of water may stay the same, in which case fresh water is being replaced by recycled water or it may decrease in line with the reduction in fresh water. In this second case, the reason for the lower fresh water use may be the replacement of a piece of equipment that requires water (eg conventional water-ring vacuum pumps) with one that does not (eg centrifugal exhauster vacuum pump). The effects of closing up on papermaking chemistry are discussed under water closure.

CMC

This is an abbreviation for carboxymethylcellulose or, in colloid chemistry, for critical micelle concentration.

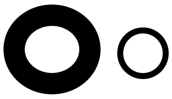
Coagulation

Coagulation is one of the terms used to describe the aggregation of particles in a suspension, but, like the term flocculation, is often used somewhat loosely to mean aggregation brought about by any added chemical. It is also used with any one of two more specific meanings:

- for the aggregation of particles brought about by compression of the electrical double layer by indifferent electrolytes or by charge neutralisation with chemicals of opposite charge to the surface. This last meaning is perhaps the most common when it refers to the use of coagulants such as aluminium compounds (alum or PAC). It is also sometimes used to describe the mode of action of low molecular mass cationic polymers (PEI, polyamines, polydadmacs, etc), but this may be more a patch mechanism than simple charge neutralisation.
- for the aggregation of particles in the primary minimum (whilst flocculation denotes particle aggregation in the secondary minimum). This is the common mode of aggregation in papermaking systems.

The term hetero-coagulation refers to the aggregation of dissimilar particles and is sometimes used for the aggregation of fillers with pulp fibre/fines. The latter is also sometimes called "deposition". Homo-coagulation is the aggregation of like particles, eg filler particles with one another or pulp fines with one another.

Coarseness



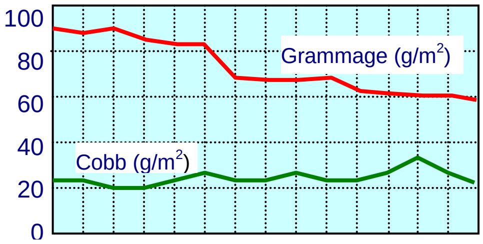
This is an important characteristic of pulp fibres and is a measure of the quantity of fibre per unit fibre length in units of mg/m. It is dependent on the fibre wall thickness and its density, but can be calculated from the length of individual fibres and the number of fibres per unit mass. The range of coarseness values is about 0.1 mg/m for narrow, thin-walled fibres such as those from birch (see representation at far right) up to about 0.5 mg/m for wide, thick-walled fibres such as those from pine (see representation at near right). Thick-walled fibres are excellent for paper stiffness, but less so for tensile strength due to their poor conformability and hydrogen-bonding ability. Thick-walled fibres also have a lower specific surface area (m^2/g), which makes them less effective at scattering light than thin-walled fibres, but the greater inter-fibre bonding of the latter negates this to some degree. The coarseness of pulp fibres is also important at the wet end in relation to the crowding number of pulp suspensions during fibre flocculation and hence to the formation quality of paper.

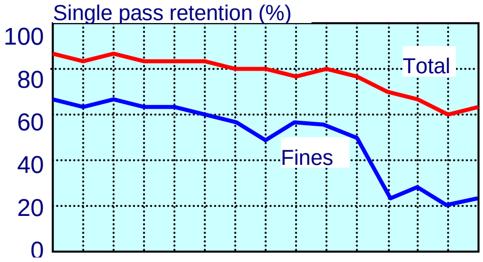
Coated papers

Conventional coated papers are those coated with an aqueous pigment suspension for improved surface characteristics in relation to its printability. The main grades coated in this way are:

- wood-free fine papers, which are aimed at the upper end of the coated papers market
- wood-containing paper in the form of light-weight coated papers, which are aimed at the lower, commodity end of the coated papers market for bulk commercial printing
- certain grades of packaging papers/boards, where the packaging is used partially for display.

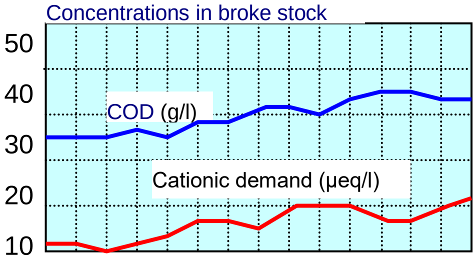
The data presented here is a useful example of some of the wet end chemistry issues on a coated paper machine, which, in this case, happens to be wood-free. Over the course of the week during which data was collected, the grammage of the base paper dropped in progressive steps from 90 to 60 g/m^2 (see figure at top right) and the type of coating applied at the coater was changed. The wet end conductivity (2-3 mS/cm) largely reflected the added alkalinity (soda ash) as the fresh water conductivity was quite low (0.4 mS/cm). The level of dissolved organics was also quite high (0.8-2 g/l COD) due to the starch added at the size press and the quite closed water system.





The observed decline in single pass retention (see second figure) was caused by several inter-related factors:

- the decrease in grammage of the base paper
- an increase in the fines content of the combined thick stock (20% to 30%) due to increased softwood refining and increased return of coated broke with a higher fines content
- an increase in the dissolved organics originating from the coated broke leading to a large shift in the cationic demand (see lower figure at right).



A low molecular mass cationic polymer was being added to the thick stock as part of a two component retention aid system with the later addition of an anionic polyacrylamide. However, the dose of the cationic polymer was kept constant and not adjusted as the cationic demand of the thick stock increased. This increase was caused by a normal change in the coating formulation that involved use of a pigment with higher dispersant content. It also evident (top figure) that the decline in fines single pass retention was accompanied by a greater variability in the degree of sizing despite a substantial increase in the size addition (from 3 to 5 kg AKD solids/tonne paper). Although not quantified directly, this would almost certainly have been due to impaired single pass retention of the size emulsion, which led to hydrolysis of the non-retained AKD and substantial deposition in the press section.

Coating

This term is used in different ways within the paper industry:

- to cover all techniques for the surface application of any substance to the pre-formed paper
- to cover all surface application techniques excluding the spray application of uncooked starch slurries or simple impregnation of chemicals in solution form (eg by a size press). This is the most common definition and will be used herein.
- sometimes used by tissue/towel mills for the application of a chemical mixture to the drying cylinder to improve adhesion and subsequent release prior to creping.

In line with the second definition above, the most common form of coating is the application of an aqueous pigment suspension to improve the paper's printability and this technique is applied to many paper/board grades. The coating system consists of a coating preparation area ("kitchen"), where the various components of the coating formulation are combined into a stable mixture and the coating machine, where the mixture is applied to the dry paper web. This may be done as part of the paper machine system (on-line coating) or separately off-line.

For aqueous pigment coating, the coating mixture comprises a number of chemical components:

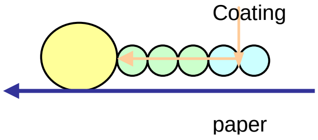
- the dominant pigment(s), which accounts for at least 80% of the coating solids
- the coating binder(s) which account for most of the non-pigment solids and hold the pigment particles together thus helping to form a smooth surface film
- chemicals to modify the rheology of the coating mix
- chemicals to control entrained gases and foam which is often associated with the binder component
- insolubilisers, to improve the resistance of water-soluble binders to water during printing
- lubricants, which have a range of effects on coating, notably improving pick-up and reducing cracking
- water retention agents for controlling the rate of water penetration into the base paper
- dispersants, which are already present in slurry-form pigments, but which may also be added later
- biocides for control of microbial problems and/or to act as preservatives
- colorants for coloured surfaces
- fluorescent brighteners.

Paper can be pigment coated on just one or both sides depending on the grade. Application rates cover the range 10-30g coating solids/m^2 on base papers that vary from about 40 g/m^2 (LWC) through wood-free fine papers (40-150 g/m^2) to boards (200-500 g/m^2). There are also other more specialised forms of coating:

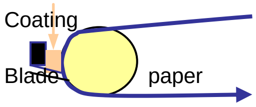
- carbonless copy papers are lightly coated with an acid clay pigment coating on one side of the paper, but the other side is coated with capsules of an oil-dispersed colour former.
- barrier coating to prevent the ingress or passage of water, water vapour, grease, oil, etc
- non-aqueous coating of silicones for release papers.

The different types of coating applicator can be classified as follows:

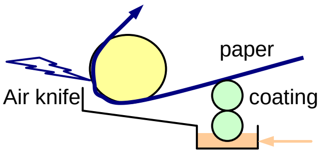
- roll coating was the first type used on-machine. It uses a number of rolls firstly to apply the coating mixture and then to ensure an even distribution across the web width as the applied mixture is transferred between the successive rolls.



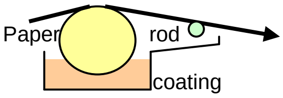
- blade coating, which applies an excess of coating mixture through the applicator head and then uses a doctor blade to remove the excess. Some blade coaters can be used to apply the coating to both sides with one head. Where the blade is separate from the applicator, the terminology trailing blade coater is used.



- air knife coating, which uses a roll or rolls to apply the coating and then a thin jet of high-velocity air to doctor off the excess.



- rod coating, which again uses a roll to apply the coating with the excess being removed by a rotating rod.



- spray coating is the latest development in coating technology and involves the use of specially-designed spray nozzles. This is a none-contact coating process that claims to give superior coating uniformity.

The coating station is always followed by a final drying stage, which often utilises techniques other than conventional steam-heated cylinders. The most common are infra-red or hot air impingement dryers, both having the advantage of being non-contacting thus avoiding potential problems from the coating layer being disturbed or of it sticking to the dryer surface.

Like size press-treated papers, coated papers have an important influence on wet end chemistry due to the nature of some of the chemicals that are recycled in coated broke. The coating pigment can contribute positively to the mineral content of the base paper, but other components of the coating formulation contribute negatively to various wet end problems:

- pigment dispersants such as polyacrylates, which contribute to the anionic trash fraction at the wet end.
- latices can contribute to wet end deposit problems in the form of white pitch.

Cobb value

This is one of the most widely-used tests for assessing the degree of paper sizing against water. This involves contacting a circular area of paper (usually 100 cm^2) with water for a defined time (most commonly 1 minute, but it can be longer) and measuring the water pick-up in g/m^2. Other techniques are the Hercules size test (HST) and tests involving complete immersion of the sample for a defined time (usually applied only to vary hard-sized papers). The 1 minute Cobb value of a waterleaf (unsized) paper may be 200-300 g/m^2, but this can be reduced to below 20 g/m^2 by the addition of sizing chemicals. A typical sizing response curve using the Cobb value is shown here.

Cockle

This is a term for local surface deformations giving a dimpled or crumpled appearance to the paper. Although their shape and size is very variable, the term "wrinkles" is often given to the same type of problem when It occurs in an elongated form. Cockles are due to non-uniform, differential shrinkage as the paper is dried and is often caused by over-drying. It can be associated with poor formation as this means that the fibre/sheet density is variable. It also seems to be more associated with pulps that swell easily and have a high fines content as such pulps tend to hold on more strongly to moisture, which leads to a less uniform moisture content at the critical point during drying (at about 60% solds content).

COD

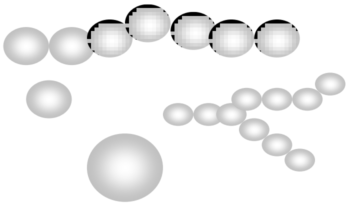
This is an abbreviation for chemical oxygen demand.

Colloidal silica

Colloidal silica is produced by controlled neutralisation and deionisation of solutions of sodium silicate. The conditions employed during this process may be varied to produce two forms of colloidal silica:

- discrete particles (silica sols of various sizes in the nm diameter region) when the pH is kept on the alkaline side of neutral or
- chains of discrete particles (ultimately silica gels) if the pH is on the acidic side of neutral.

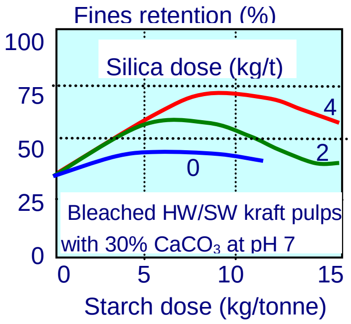
Most of these products are linear aggregates, but branched structures may also be produced (see representations at right). Different forms of colloidal silica have been used for many years in the aggregation of fine particulates (eg the use of "activated" silica in water treatment), but it was not introduced into the papermaking process as a retention/drainage aid until the early 1980s. At this time, there was one major supplier (Eka Chemicals with its Compozil system), but there are now several suppliers offering somewhat different variants on the basic composition.



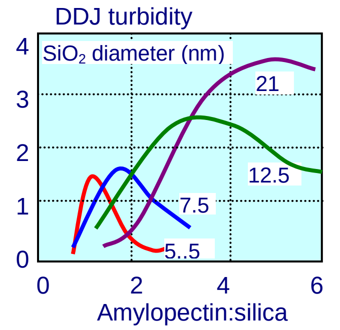
The most commonly-used silica sols have an average diameter of about 5 nm with a surface area of about 500 m^2/g (see this table for comparison of particle numbers for various papermaking materials). The surface charge is negative because of the presence of ionisable silanol (Si-OH) groups from the reaction of surface oxygens with water. As the silanol groups are weakly acidic, their anionic character depends on pH with quoted values of 0.5-1 meq/g in the neutral pH range. The chemical character of colloidal silica may be modified to give greater anionic character under acid conditions. The branched silica products have a much higher surface areas (1200 m^2/g) and, because of their strong interaction with water to produce gels, they have to be prepared on-site as they are only stable at much lower concentrations (about 1% solids) compared to the normal colloidal silica products (10-15% solids).

The introduction of Eka's Compozil system was the first of the so-called micro-particle systems, although it is now labelled, more appropriately, as a nano-particle system. All of these systems, whether nano-particle or micro-particle, aim to give not only maximum single pass retention of fines, but also maximum drainage allied to good paper formation and strength (see these diagrams for further discussion of this aspect). The strength improvement aspect comes from the fact that the use of colloidal silica as a retention/drainage aid requires at least one other component to make it effective and, in its original applications, this was always cationic starch. This chemical was already commonly used as a dry strength aid on the wood-free fine paper machines on which colloidal silica was first applied.

A typical example of the effect of colloidal silica with cationic starch is shown in the figure at right in a simple DDJ experiment at 1000 rpm stirrer speed. In such applications, the starch dose would be dictated by paper strength requirements and the dose of silica would be adjusted to optimise retention and, where required, drainage. The mechanism of this retention system involves penetration of the starch-flocculated suspension by the vast number of anionic silica particles to create a 3-dimensional structure with silica bridges (see generic picture here).

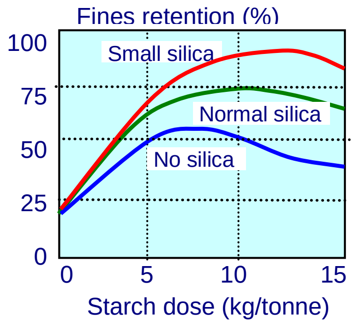


Source: Larsson at Pira Conference
on Retention Aspects of
Wet End Chemistry, 1984 .



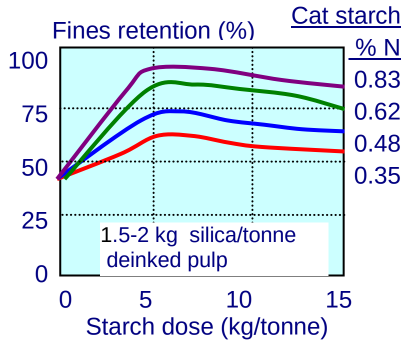
Source: Au and Johansson in Pulp Paper Canada, 1993, 94, 6, T173-176.

Given the various structural possibilities mentioned above, a fundamental issue with colloidal silica is to define its optimum particle size and configuration. The figure at left indicates the degree of interaction (as judged by the turbidity, where a low value indicates a strong interaction) between various different-sized colloidal silicas and cationic amylopectin. It is evident that the interaction increases as the silica particle size is reduced (in line with the increased surface area around the particles) and this is borne out by the performance of smaller colloidal silicas brought onto the market in the mid-1980s (see figure at right). However, not all mills used or wanted to use cationic starch and some countries (eg Japan) simply do not use much starch in papermaking, but prefer to use other strength additives. This led to the development of colloidal silica systems using other flocculant components, notably polyacrylamides (and, where high strength is required, cationic guar gum) and also to further development of the form of colloidal silica itself and of the auxiliaries used with it.



Source: Andersson at Pira Conference "Use of minerals in papermaking" Manchester, 1997

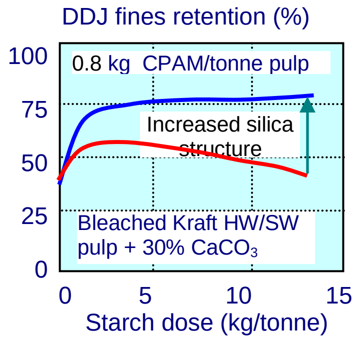
From the early days of its use in largely wood-free neutral papermaking systems, colloidal silica had often employed a third component alongside cationic starch. At that time, this was most likely to be alum or possibly polyaluminium chloride, the role of which was to neutralise or fix the relatively small amounts of anionic trash in the furnish and thus allow the cationic starch to function with its full cationicity undiminished through interaction with the anionic trash substances. This issue became more important with furnishes containing higher levels of anionic trash such as wood-containing and recycled grades. Such systems also contained much higher levels of electrolytes than wood-free systems and this reduced the molecular extension of the cationic starch chains. This was tackled by using starches of higher cationicity than used in wood-free systems, the benefits of this being shown in the figure at left for a deinked pulp



Source: Andersson at Pira Conference "Use of minerals in papermaking" Manchester, 1997

Today, colloidal silica systems are probably best described as having three essential components - the colloidal silica, a charge neutraliser for anionic trash and a flocculant where the amount and type of each need to be optimised for each type of furnish. Today, the component for dealing with the anionic trash is most commonly a cationic polymer, which is also thought to perform another function when polyacrylamides are used with colloidal silica. This is their so-called "blocking" action, whereby their adsorption on the particle surface prevents the polyacrylamide adopting a flat adsorbed conformation (see this picture and other pictures under bridging) as it might when the charge attraction is high (ie when either the polyacrylamide and/or the surface are highly-charged).

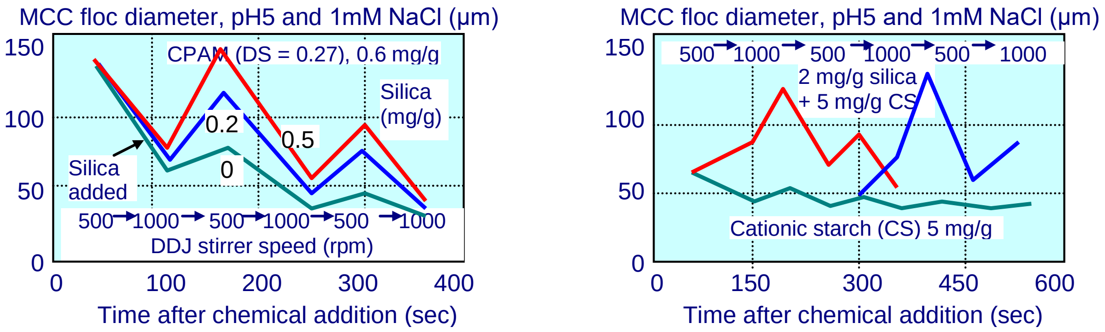
Because of their different structures, cationic starch and polyacrylamides are often used with different types of colloidal silica for optimum performance. The dominant starch polymer, amylopectin, has a very high molecular mass combined with a highly branched structure, whereas polyacrylamide also has a high molecular mass (albeit less than the amylopectin), but with a linear conformation. It has been found that the polyacrylamide-based systems give the best results with a highly-structured silica, whereas the degree of structuring has little effect when cationic starch is used. This is illustrated in the figure at right where the highly-structured silica has a chain length of approaching 40 nm. This effect would appear to have something to do with the greater separation between the polymer chains in the linear polyacrylamide than in the highly-branched amylopectin starch fraction.



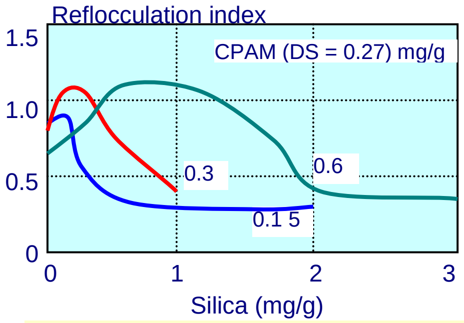
Source: Andersson in Nordic Pulp Paper Research J., 1996, 1, 15-21.

The other important aspect of any retention aid system is its response to the changing shear levels on the paper machine (most of the work described above having being done at 1000-1200 rpm stirrer speed in a DDJ). Data from some interesting work comparing a cationic starch with a cationic polyacrylamide in terms of their shear resistance and reflocculation ability (by varying the impeller speed in a DDJ) is shown in the two figures below (see figure here for effect with various polyacrylamides on their own).

It is evident that the addition of colloidal silica enhances flocculation of the micro-crystalline cellulose (MCC) up to a dose of 0.5 mg/g, but a higher dose of 1 mg/g (not shown) caused a drop in flocculation, possibly due to charge reversal. The right-hand figure shows results for the cationic starch (DS = 0.04) when the colloidal silica is added either soon after the starch or somewhat later, but the results are comparable in both cases, indicating excellent reflocculation after removal of the high shear level.



Source: Swerin et al in J.Pulp Paper Science, 1997, 23, 8, 374-381.



Source: Swerin et al in J.Pulp Paper Science, 1997, 23, 8, 374-381.

The data from these experiments can be re-plotted in the form of a reflocculation index, which is the ratio of the floc size after and before the first high shear period at 1000 rpm. This is shown at left for the same cationic polyacrylamide as in the figure at left above, but at three different dose levels (0.15-0.6 mg/g). This confirms that colloidal silica enhances the reflocculation ability of cationic polyacrylamide, but the optimum silica dose moves to higher levels as the polymer dose increases. Comparative data is shown here for the same polyacrylamide with bentonite and here with polyethyleneimine.

All of the results shown in this section on colloidal silica have demonstrated its effectiveness in improving fines retention, but its impact on drainage is equally or, in some cases more, important. One example of this is shown here, where colloidal silica overcomes the poor drainage associated with high doses of cationic starch on its own. The beneficial effect of colloidal silica on drainage has been demonstrated in many papermaking systems. Another valuable benefit of using colloidal silica with cationic starch is that it enhances starch adsorption and hence increases starch's single pass retention. In systems containing starch recycled from broke, the retention of cationic starch has appeared to exceed 100% due to the retention of some recycled non-cationic starch. These interactions with starch allied to better particulate retentions and improved drainage are particularly important on recycled machines making grades such as liner/fluting in very closed water systems. Such applications now represent the second largest sector using colloidal silica with wood-free fine papers still heading the list.

Colloid chemistry

Colloid chemistry deals with the interactions between materials that have a size from about 1 nanometre (nm, a billionth (10^{-9}) of a meter) to about 1 micron (μ, a millionth of a meter), ie with interactions between large molecules and small particles. This is not a rigid definition of the size range covered by colloid chemistry, as there is a gradual change at the upper colloidal boundary with materials in bulk suspension and at the lower boundary with smaller molecules in true solution.

There are three generic types of colloidal system:

- ❑ “simple” colloidal dispersions of the dispersed phase in the dispersion medium, such as:
    - emulsions of one liquid in another, such as milk
    - foams in which fine gas bubbles are dispersed in a liquid
    - dusts or aerosols in which fine particles or liquids are dispersed in a gas
    - fine particulate solids dispersed in a liquid such as paint
- ❑ true solutions of macromolecular materials such as starches and synthetic polymers in water
- ❑ association colloids such as solutions of surface active materials which form dissolved aggregates (micelles) above a certain concentration.

In papermaking, colloid chemistry occurs to some degree in most areas:

- ❑ in wet end chemistry, where most substances (other than pulp fibres) are colloidal
- ❑ in coating, which is a 100% colloidal system
- ❑ in deinking, which is involved with the removal of largely colloidal-sized substances
- ❑ in mill wastewater treatment, which approaches a 100% colloidal system as mill wastewaters tend to contain the more-difficult-to-retain fines and dissolved solids.

In all of the above systems, there may also be colloidally-dispersed gases present as well as particulate and dissolved solids. The papermaking furnish contains particles with an enormously wide range of particle sizes and the relationships between particle size, particle shape, particle number and particle surface area are covered under particle characteristics. A key application of colloid chemistry to papermaking is in terms of understanding the interactions between these particles, which involves consideration of the attractive van der Waals forces and the various repulsive forces. Another important facet of colloid chemistry is the process of adsorption, which is particularly relevant to wet end chemistry.

Colloid protection

This is an alternative term for steric stabilisation.

Colloid titration

This technique (also known as polyelectrolyte or just polymer titration) is one of several charge titration techniques used in papermaking. Colloid titration was developed in Japan in the 1950s and was originally used by chemical manufacturers to assay the charge density of organic polymers. Polymers of opposite charge interact together via the ionic groups on their backbone to form polymer complexes (symplexes). This interaction may or may not be stoichiometric depending on the ability of the polymer chains to conform close enough to one another for the charge groups to interact, ie the degree of charge neutralisation depends on polymer chain flexibility, relative charge densities, electrolyte concentration, mixing conditions, etc. Generally however, it has been found that, provided the titration is carried at zero ionic strength, the charge interactions do have a 1:1 stoichiometry.

In this classical procedure, a polymer of unknown cationicity is titrated with a standard anionic polymer using the dye, toluidine blue, as the end-point indicator, which turns pink-red in the presence of excess anionic polymer. The anionic polymer used is nearly always potassium polyvinyl sulphate (KPVS), but others (such as sodium polyethylene sulphonate [NaPES]) have also been tried. For assaying an unknown anionic polymer, this may be titrated against a standard cationic polymer or an excess of standard cationic polymer added and the excess charge back-titrated with the anionic polymer.

Essentially, the same methodology is used for papermaking samples that have an unknown titratable charge. Measurement of the cationic demand involves titration with any cationic polymer (such as a polydadmac or Polybrene), but it makes sense to use the same cationic polymer planned for full-scale use for this purpose on the paper machine. The anionic demand can also be measured and the two demands brought together to calculate the net demand (anionic or cationic) or the colloid titration ratio (anionic demand/cationic demand). However, after a good deal of arithmetical manipulation in the early days of applying this basic technique to papermaking samples, it was concluded that only the actual demand (usually cationic, but the anionic demand may be more significant in a few systems) has any practical relevance to real papermaking.

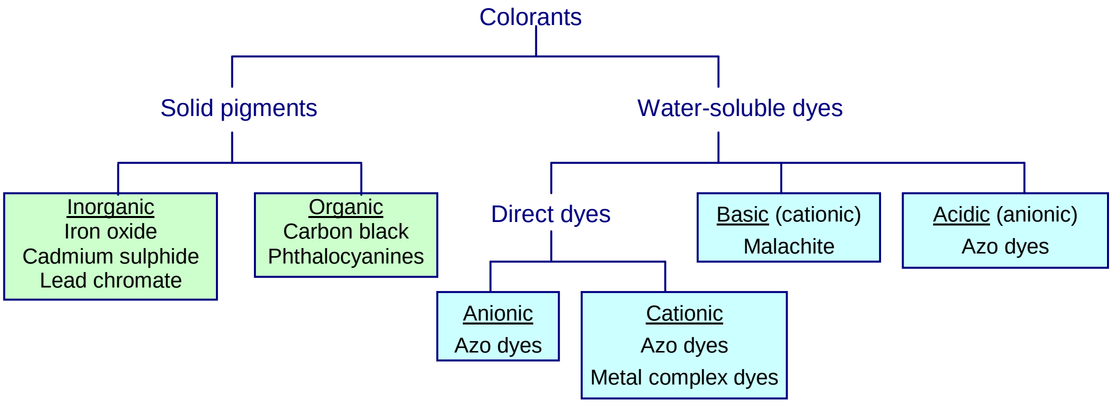
This technique is principally used today to measure the cationic demand of the liquid phase, but it can also be applied to the whole sample to measure the demand of the total matrix and then, by difference, that of the liquid phase and the particulates separately. It needs to be made clear that the demands of the two fractions (solubles and particulates) are very different in terms of charge neutralisation. For solubles, the reaction will terminate at or near to the point of charge neutralisation, but polymer adsorption beyond the point of zero zeta potential is likely to occur on the particulates due to there being other (non charge-related) adsorption mechanisms. This probably explains the fact that the polymer-titrated charges shown in the table are generally higher than the charges calculated from titrations with other materials.

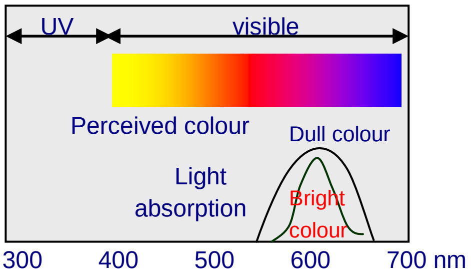
Of course, when such cationic polymers come to be used on a paper machine, typically in the thick stock, the presence of the particulate matrix is very significant as there will be competition between adsorption of the cationic polymer on the particulate surface and interaction with dissolved anionic polymers. For control of anionic trash, it is critical that the added cationic polymer interacts preferentially with the anionic trash before any adsorption on the particle surface. This information cannot be obtained from a cationic demand measurement, but requires additional measurements of the changes in particle charge when the polymer is added to the whole sample (see here for an example using polydadmacs and PAC).

This classical colloid titration method using the colorimetric end-point is one of several possible charge titration techniques, but is less used than it used to be. One reason for this is that the end-pint colour change can be difficult to see clearly in some papermaking samples, but the main reason is the greater ease of use for the method based on the streaming current detector end-point. Nevertheless, the colloid titration technique does feature within ABB's WIC on-line monitoring system.

Colorants

Colorants are used in papermaking to modify the natural colour of paper. This can be done either at the wet end or by surface application using either solid pigments or water-soluble dyes, as shown in the classification scheme below. A special form of colorants are the dyes used in carbonless-copy papers and in thermal (fax-type) papers.





All atoms and molecules absorb electromagnetic radiation through electrons being excited from one energy level to another. In many cases, this energy difference is outside the visible region of the electromagnetic spectrum, often in the shorter-wavelength ultra-violet. In the case of colorants, the energy difference corresponds to that available from visible light. Depending on the distribution of wavelengths where visible light is absorbed, colour is perceived as a result of the light re-emitted. The sharpness of the absorption peak determines the purity of the resultant colour, a broad absorption peak giving a less-bright, duller colour than a sharp peak.

Colorants are sometimes rated in terms of their tinctorial value, which simply means the strength of colour produced per unit mass. Dyes are better in this respect than coloured pigments.

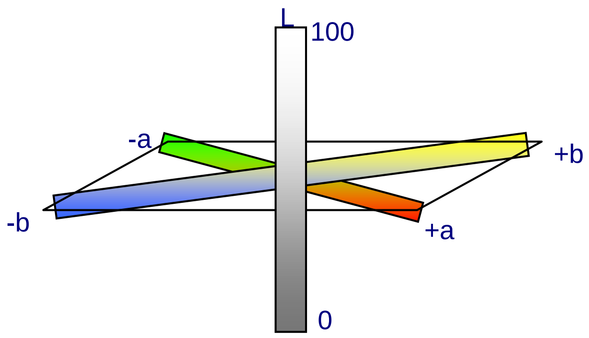
Colour

The colour of paper is affected to some degree by the colour of all the raw materials used in its manufacture, but most notably by the colour of pulps, which vary from various degrees of brown through to white and of mineral fillers, which have various levels of whiteness and brightness. What might be called the natural colour of the paper (ie in the presence of pulps and filler only) is deliberately changed through the use of colorants and fluorescent brighteners.

The original measurement of colour goes back to the work of Maxwell in the 19th century who showed that most colours could be made by the mixing of three primary colours, in his case of red, green and blue. He devised a colour triangle to define any particular colour and this could be used to match most, but not all, colours. In view of this shortcoming, a new system was later developed by the Commission Internationale d'Eclairage (CIE) based on three artificial colours, the so-called tri-stimulus values - X (strong red component, Y (green/yellow component) and Z (strong blue component). The colour at any wavelength can then be represented by various proportions of these three colours (say, x, y and z respectively) so that x + y + z = 1. A plot of x versus y gives the CIE chromaticity chart, from which z can be calculated (z = 1-x-y).

Due to the bunching of certain colours in this chart, it was not easy to use it for colour matching so a new system was devised and this has been used since the mid-1970s. This is the CIE L*a*b* system (the asterisks differentiate it from the similar Hunter Lab system), which is based on the findings that the human perception of colour is based on a distinction between six main characteristics and these are built into the L*a*b* values with the resulting CIE - L*a*b* colour space represented by the diagram shown here:

- the L* value is derived from the Y tri-stimulus value and is a measure of lightness/darkness
- the a* value is derived from the X and Y values and is a measure of red to green
- the b* value is derived from the Y and Z values and is a measure of blue to yellow.



When a* = b* = 0, the sample is said to be achromatic (no colour) and its L value then determines its balance of white and black (greyness).

There are other colour classification systems such as the Munsell System which describes each colour according to three attributes:

- hue is the quality that distinguishes one colour from another (eg blue from yellow) and is equivalent to the position in the a-b colour space.
- value, which is the lightness-darkness and is equivalent to the L position in colour space
- saturation (or chroma or colourfulness) is the depth or vividness of a colour and is measured by the magnitude of the measurement parameter.

The colour of an object may appear to be not the same under different light sources and this is known as metamerism. There are a number of standard illuminants to simulate different light sources, two examples being illuminant A for tungsten light and the D series of illuminants (eg D65 for daylight).

Conductivity

This is the ability of water to carry a current and is synonymous with the term "specific conductance". The conductivity is the current carried per unit area of the liquid through which the current is passing per unit potential gradient. The normal units are Siemens/m where the Siemen is a mho (reciprocal ohm or amp/volt). Conductance is measured in Siemens and is the reciprocal of resistivity measured in ohms. Conductometric titrations with sodium hydroxide are used as one of several possible charge titrations to quantify the charge on pulps.

In dilute solutions, the total conductivity can be estimated from the sum of the specific ion conductances, which are dependent on the ion's size and charge. For example, the conductivity of a 1 g/l potassium chloride solution, often used to calibrate conductivity meters, is 1.7 mS/cm at 25^{o}C. The relationship between concentration and conductivity is not linear due to increased ionic interactions at high concentrations, eg the predicted conductivity of a 1 g/l KCl solution is about 2 mS/cm based on the ion conductivities of potassium and chloride in very dilute solutions. A rough "rule-of-thumb" for natural waters is that the conductivity in mS/cm is about 1.4 times the total dissolved salts in g/l. Conductivity increases with raised temperature by about 2% per degree due to the decrease in the viscosity of water. Conductivity is also related to the more fundamental chemical term, ionic strength.

The ability of deionised water to carry an electrical current is limited by the very small quantity of ions (protons and hydroxyl ions) present, its conductivity being about 0.05 µS/cm. The much higher conductivity of natural fresh waters (up to about 0.5 mS/cm) is due to the presence of dissolved electrolytes, which originate from various sources. In papermaking systems, the measured conductivity is due to the presence of electrolytes from fresh water and other sources. The contribution of charged polymers is small due to the low specific conductance of the large molecules.

The range of conductivity levels in papermaking systems is from about 0.5 to around 10 mS/cm (see these values for several machines with fully-closed water systems)and this is discussed further under electrolytes. There is one direct effect of conductivity itself, which is on the level of corrosive activity.

Conformation

This term is used to describe the 3-dimensional structure of chemicals. In papermaking, it is mainly applied to discussions of the structure of various polymers (eg cellulose) in terms of the position and extension of the polymer chains. Conformability is used to describe the ability of cellulose fibres to align themselves with one another and this is dependent on fibre flexibility and the degree of fibre swelling.

Consistency

This is the very commonly-used term for the mass concentration of particulate solids in the papermaking stock or water. Particulate solids are measured at most mills by manual sampling and laboratory analysis, but increasingly by on-line sensors to give real-time information on consistencies and wire retentions. The total consistency is determined in the laboratory by drying the whole sample at 105^{o}C to give the percent solids by mass (normally done only on thick stock samples where the contribution from the solubles is relatively low) or by filtration through an appropriate medium to give the % by mass, if the original sample was weighed, or a g/l figure if the original sample was measured by volume. The most common locations for consistency measurement are the thick stock, thin stock at the flowbox and whitewater passing through the formation wire.

If required, the total particulate solids can be analysed further for its component fractions:

- ❑ the fines content may be determined using the standard dynamic drainage jar technique or by using the Bauer-McNett classifier
- ❑ the ash content of the dried solids is frequently determined, mainly at mills using fillers, in order to quantify the retention of the more-difficult-to-retain mineral filler fraction
- ❑ specific inorganic components of the particulate solids can be determined by direct chemical analysis. Calcium carbonate can be determined from the ash measurement as above or by acidification followed by one of the normal methods for soluble calcium. A carbon dioxide specific electrode can also be used under controlled pH conditions, which releases an amount of CO_2 proportional to the carbonate content.
- ❑ titanium dioxide can be analysed directly once released by acidification of the solids and then treated with hydrogen peroxide to form an orange/red-coloured titanium (VI) compound.
- ❑ pulp components (cellulose, hemi-cellulose, lignin and extractives) can be measured using conventional pulp analysis techniques, but only the latter parameter is normally of value in wet end chemistry work (in connection with pitch problems).
- ❑ specific functional chemicals such as sizes can be analysed, but this depends on the availability of suitable techniques and analytical expertise at the mill. This is rarely done apart from during special research studies, but analyses might be undertaken for:
    - rosin, which can be measured using the standard TAPPI extraction method, but there are no fully proven, simple methods for other sizes such as AKD and ASA.
    - starches, which can be determined by the colorimetric or enzymatic techniques, in which the whole sample (rather than just the filtrate) is pre-treated with the amylolytic enzymes
    - wet strength agents, which can be assayed via their nitrogen content using the Kjeldahl digestion technique, but other sources of nitrogen are often present.

An important aspect of consistency measurement is the possibility for on-line monitoring around the formation wire in order to control the stock's retention characteristics. This requires the reliable measurement of consistencies below 10 g/l, which is below the lower limit of the consistency sensors based on shear resistance that are widely used on thick stock samples. Simple optical sensors based on light scattering were tried in the 1970s, but were unable to cope with the complex particulate matrix present on many machines. The first successful on-line retention system was developed by the Swedish company Chemtronics (now part of Eka Chemicals within Akzo Nobel) and was first installed on a wood-free fine paper machine in the mid-1980s.

The success of this system was due to the recognition that at least two sensors (in this case, one based on polarised light and the other on infra-red) were necessary for measuring total consistency at most mills. The reason for this is simply that each component of the particulate solids has a different attenuating effect on the light passed through it, but, if the particulate solids can be broken down into just two light-attenuating fractions (say, fibre and filler), then two sensors (or measurement of the light-scattering from one light source, but at two different angles) are necessary. Machines with more than one filler, each with different light-attenuating properties, will probably need more than two sensors.

Today, on-line consistency/retention monitoring systems are widely used for control of one of the components within the retention aid system. They are now available from a number of suppliers, the main ones being:

- ❑ Chemtronics Monitrol system

  This now uses only one laser light source, but several signals are obtained to provide fibre and filler consistencies (and calculated retentions) and an index of stock flocculation. Only one sensing head is used with a standard sampling sequence of flushing water, flowbox and then whitewater. Each sampling cycle takes no more than 4 minutes. The Chemtronics system has now been installed on over 100 paper machines throughout the world. There is also a dedicated type of sensor for monitoring total consistency and ash content for repulped broke.

- ❑ Metso Automation kajaani RMi system

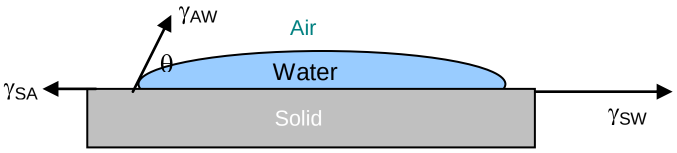
  This current system has developed from previous Kajaani RM-200 units developed for wood-free and wood-containing furnishes. It measures total/ash consistencies and flocculation level and is probably the most widely-installed system with over 300 paper machines using it world-wide, of which about 100 are on closed loop control.

- ❑ BTG RET system

  This system uses an optical sensor with a unique measurement technique (the Peak method) to separate the influence of intact fibres and fine particles on the transmitted light. In this, the peak signal is taken as a measure of the fibres and the average signal as a measure of the fines.

Contact angle

The situation where a liquid (in this case, water) is in contact with a solid surface (or a second liquid) is illustrated in the figure at right.



The relationship between the various interfacial energies for a flat surface can be described by the following (Young's) equation, which assumes that surface forces can be represented by surface tensions acting in the direction of the surface:

$$\gamma_{SA} = \gamma_{SW} + \gamma_{AW} . \cos\theta$$

where γ_{SW} = interfacial energy between the solid and water
γ_{SA} = interfacial energy between the solid and air
γ_{AW} = interfacial energy between air and water
θ = contact angle

The contact angle is a measure of the cohesive forces within the liquid versus the liquid-solid adhesive forces and is zero when the surface is fully wetted by the liquid. Contact angles greater than zero imply some degree of non-wetting, which is always the case in practice. In the case of water as the liquid, it increases from zero for a hydrophilic surface to 180° for a hydrophobic surface, but, in practice, is always somewhere between these two extremes. The interfacial energy between the solid and water is thus maximised as the contact angle increases and this is the intended consequence when paper is sized with hydrophobic materials. Intermediate values of the contact angle determine the degree of surface wetting or spreading.

Conversion

This term has two principal meanings in papermaking:

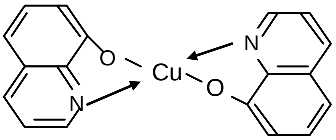
- the in-mill conversion of starches into a soluble form
- the conversion of papers into their final form for use. Conversion may take place at the same site as papermaking or elsewhere. Examples of such processes are:
    - the conversion of packaging materials into boxes, eg the combination of linerboard and fluting medium into corrugated cases. This is important in relation to the recycling of used corrugated cases as conversion involves the use of adhesives, which cause problems on the paper machine.
    - the conversion of tissue paper into tissue products such as toilet tissue. This may also involve the use of adhesives, but this has no implications for papermaking as tissue products are not recoverable.
    - the conversion of printing/writing grades from reel form into specific products. These are purely mechanical processes such as slitting, re-reeling and cutting.

Co-ordinate bond

This is one of the three types of chemical bond, this case being where the bonding electrons are donated by only one of the bonding entities and then shared between them. This type of bonding is not common in chemicals used in papermaking, the best example being the interaction of aluminium ions in alum with water molecules.

Copper

This element heads Group 12 of the Periodic Table. It is present in two types of papermaking raw material:



- copper-based fungicides such as the complex, copper-8-hydroxyquinolinate (also known under various other names such as oxine-copper) with the formula shown at right. This is well-known as a wood preservative and is also used for this purpose in papermaking.
- copper sulphate, which is used as a catalyst with hydrogen peroxide in the production of thermo-chemically-converted starches
- some dyes such as the anionic direct dye shown here.

Corn starches

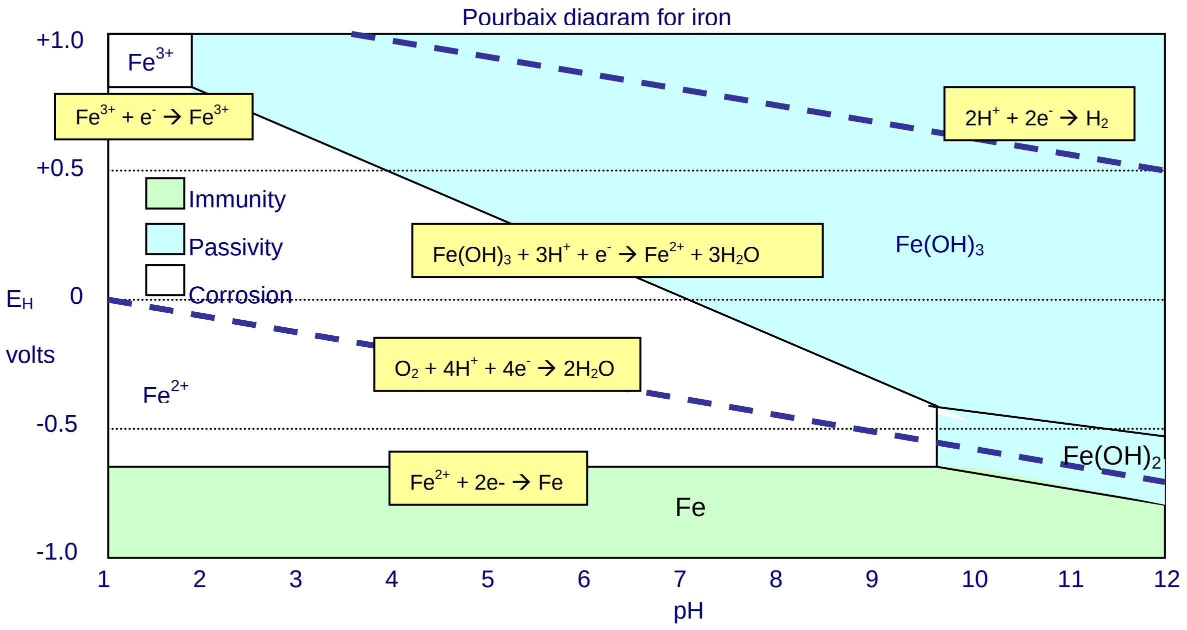
These are also called maize starches and are one of the most common types of starch used in papermaking. They have a lower amylopectin content than potato starches and contain some fatty material (see this table for comparison with other starch types). The shape of corn starch granules is a mixture of round and polygonal particles with a mass average diameter of about 15 µm. There is one unique type of corn/maize starch, waxy maize, which is 100% amylopectin.

Corrosion

Corrosion is the destructive breakdown of a material by reaction with its local environment. In papermaking, the main concern is the corrosion of metals that form the tanks, pipes and the various parts of the paper machine itself, but atmospheric corrosion may also be important due to the high humidities in many machine houses. Corrosion of metals is a spontaneous electrochemical process, in which the corrosion process may be driven by the potential difference between:

- dissimilar metals, where the metal with the more negative redox potential will act as the anode, eg iron (E_H^o = -0.44 volt) is anodic against copper (E_H^o = +0.16 volt)
- different areas on the surface of the same metal, the potential difference being due to:
    - surface inhomogeneities such as stress cells, where a part of the metal structure is at a higher stress than and is therefore anodic to other parts of the same metal or at grain boundaries leading to inter-granular corrosion.
    - liquid phase inhomogeneities such as concentration cells, where the concentration of a substance participating in the corrosion reaction (eg dissolved oxygen) varies within the system and thus sets up a potential difference between these sites. In the case of dissolved oxygen, corrosion is greatest where the dissolved oxygen concentration is lowest as this area is anodic to areas where the concentration is higher.

A useful way of looking at the thermodynamics of corrosion reactions is the potential-pH diagram, often referred to as a Pourbaix diagram. In this diagram, the boundary conditions are set by the pH/E_H domains where water is unstable through either being oxidisable to oxygen or reducible to hydrogen.


Pourbaix diagram for iron

For any particular concentration of a metal, the diagram divides the pH-E_H space into three regions where the metal is immune from corrosion, prone to corrosion or tends to form a thin passive surface film, usually of an oxide. This is illustrated in the Pourbaix diagram below for iron, from which is evident that iron is corrosive over the common range of conditions found in papermaking systems.

Pourbaix diagrams are useful is defining the equilibrium conditions for corrosive reactions, but corrosion reactions are often not at equilibrium for kinetic reasons. The actual corrosion rate can be measured by determining the anodic and cathodic polarisation curves, where the potential often increases linearly with the logarithm of the applied current. This relationship is a measure of how the rates of the anodic and the cathodic reactions are retarded by various environmental factors such as the concentration of metal ions, dissolved oxygen, etc (referred to as concentration polarisation) and/or by surface processes such as adsorption, film formation, etc (referred to as activation polarisation). The hydrodynamics of the system also play a key role in determining the corrosion rate as the mass transfer of cell reactants and cell products are often the rate-limiting step. A fairly common set of conditions in papermaking is the initial slowing down of a corrosion reaction due to the polarisation from the build-up of hydrogen gas. However, the corrosion reaction can be depolarised under aerobic conditions by dissolved oxygen or under anaerobic conditions by sulphate-reducing bacteria.

Corrosion can be controlled by different conceptual approaches:

- the use of inherently more corrosion-resistant materials
  Cast iron structures are particularly prone to corrosion due to the presence of carbon particles whereas stainless steel has a lower carbon content and incorporates chromium and nickel which give a superior oxide film for protection.
- the use of barriers to protect the underlying metal, which can take various forms:
  - galvanising iron or steel with zinc
  - anodising surfaces (eg aluminium) to produce a protective oxide layer
  - Applied coatings such as paint, bitumen, lacquers, etc.
- manipulation of the surface potential in which the metal is either
  - made the cathode and thus immune to corrosion (cathodic protection) or
  - made the anode and thus passive towards corrosion (anodic protection).
- modifying the chemistry of the aqueous phase by:
  - changing the pH to bring the surface into an immune or passive region
  - changing the pH so that a thin layer of calcium carbonate is formed
  - adding corrosion inhibitors, of which there are many types (sodium benzoate, organic film-formers, phosphates, chromates, etc).

Substances present in papermaking waters can accelerate corrosion and these substances represent a sub-set of the wider range of problematic substances. As noted above, another set of problematic substances that can contribute to corrosion is the set of substances supporting microbial activity. Firstly, the aerobic bacteria remove dissolved oxygen (DO) and create localised corrosion cells at different DO levels. Once the DO is depleted, anaerobic heterotrophic bacteria create acidity in the form of organic acids and sulphate-reducing bacteria can consume hydrogen, thus depolarising the corrosion cell. Once the sulphides are released to the mill atmosphere as hydrogen sulphide gas, this presents further corrosion problems either directly (eg by reacting with silver electrodes in control gear) or after microbial oxidation to sulphuric acid.

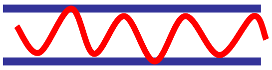
The ionic quality of the process waters also affects corrosion in several possible ways:

- overall conductivity through simply increasing the electrical carrying power of the liquid phase surrounding the corrosion cells
- chloride, which is often implicated in the pitting or crevice corrosion of stainless steel, but this requires concentrations at the high end of the normal range
- sulphate in terms of the supply of ions for microbial reduction
- thiosulphate can cause pitting corrosion of stainless steel (304 grade) at concentrations below 50 mg/l.

It should be noted that concentrations well above the measured whitewater or stock concentrations can occur in splash zones during drying-out periods. Corrosion problem areas at paper mills have evolved over the years in response to changes in construction materials. With the move away from brass/bronze to some form of synthetic organic (eg polyester) formation wire, problems of dezincification have disappeared, although this can still occur with couch and suction rolls. Stainless steel has become the construction material of choice for many mills with the corrosion-resistant 316 grade, despite its high cost compared to the 304 grade, often being used. 316 stainless steel contains 2-3% molybdenum, which, in addition to the nickel and chromium also in the 304 grade, gives extra protection against chloride pitting.

Corrugated cases

These are the packaging boxes that result from the converting of linerboard and fluting. There are various constructions using 1-3 layers of fluting between 2-4 layers of liner. The flutes have different sizes with several standard grades (A, B, C and E) and several non-standard ones such as mini, micro and extra coarse.



In the manufacturing of the case, the fluting is firstly heated and then pre-steamed to soften the lignin. The actual corrugation is conducted at high temperature followed by the gluing to the outer liner, one side at a time. The adhesive is applied to the flute tips at a dose of 4-8 g/m^2 (thickness 0.1-0.25 mm) and then contacted with the liner. Temperature is very important during application of the adhesive. The water absorbency of the fluting and liner is critical.

Unmodified starch is the most common corrugating adhesive, but modified starches and other materials may be used. There are a number of different techniques to prepare the starch adhesive, but a basic sub-division is between two systems depending on the degree of initial starch cooking:

- the so-called carrier systems (often referred to as Stein-Hall process), where the adhesive (starch) is present in two forms:
  - the primary (carrier) portion of the adhesive, which accounts for 10-20% of the total starch. This is a fully-cooked starch solution containing some caustic soda to allow gelatinisation of the starch granules at lower-than-normal temperature and borax to improve initial tack and shear stability. The resultant solution is then diluted with water to cool the solution and arrest the gelatinisation process.
  - the secondary starch, which accounts for 80-90% of the total starch. This is added as a powder and begins to gelatinise before application depending on the temperature of the primary starch solution.

  The carrier system provides a blend of initial adhesion and water retention with strong final adhesion to both fluting and liner.

- the no-carrier systems

  As the name suggests, these starches contain no cooked starch so the starch powder has to have a well defined and uniform rate of reaction with caustic soda. These are typically maize (corn) starches with a gelatinisation temperature just over 60°C.

Most formulations can be supplied in a pre-mixed form for ease of preparation. The solids content of the final adhesive is 20-25% and can incorporate other additives:

- a preservative to stop microbial activity which will degraded the starch's functionality
- a wet strength agent to give the set adhesive some resistance to water.

Corrugating medium

This is an alternative name for fluting medium.

Covalent bond

This is one of the three types of chemical bond, in this case where two atoms share electrons to form a stable configuration through overlapping of their electron orbitals. This sharing of electrons can only occur when neither of the bonding atoms is strongly electrophilic or nucleophilic as such atoms would tend to form an ionic bond. In practice, this means that this type of bond is restricted to elements towards the middle of the Periodic Table, the best example being the enormous range of organic compounds based on carbon. Even with covalent bonds, the electrons may not be shared equally, giving rise to some ionic character in many covalently-bonded chemicals.

In fact, the distribution of the bonding electrons is only uniform when the two atoms are the same, as in hydrogen (H - H) or chlorine (Cl - Cl). If we take the simple case of hydrogen chloride (H - Cl), chlorine is strongly electrophilic, so the bonding electrons are displaced towards it, giving the chlorine atom a slightly negative charge and, in order to maintain overall neutrality, the hydrogen atom a slightly positive charge. This is usually written as shown at right with the arrow indicating the direction of electron displacement.

$$\overset{\delta^+}{H} - \overset{\delta^-}{Cl} \quad \text{or} \quad \overrightarrow{H - Cl}$$

Because of the charge separation, such molecules have a dipole moment. This type of charge separation is also the underlying factor behind the hydrogen bond.

Creping

This is the process of introducing small folds or compressions into the paper and is usually carried out on the Yankee cylinder for tissue/towel grades to improve their bulk and softness. The creping of the sheet occurs when the dry web is removed from the cylinder by the creping doctor blade. Most papers will adhere naturally to the cylinder surface, but adhesion and hence the quality of the creping can be improved by the addition of chemicals either at the wet end or by direct spraying onto the cylinder. This creping mixture may contain three components:

- an adhesive such as a polyamide, polyaminoamide resin or polyvinyl alcohol
- a release agent that is more hydrophobic in character than the adhesive such as emulsified mineral oils, fatty acid esters and polyphosphates
- a wetting agent, usually a surfactant.

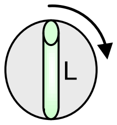
Doses are normally below 5 mg per m^2 of cylinder surface, but are much higher (around 50 mg/m^2) for creping tissue after through-air drying.

Crowding number

This is a useful term in looking at the flocculation characteristics of fibre suspensions.

$$\text{Crowding number} = \pi/6.\ L^2/C.C_m \ = 2/3.(L/D)^2.C_v$$

where L = fibre length (m), C = fibre coarseness, C_m = fibre mass concentration (kg/m^3), D = fibre diameter (m) and C_v = fibre volume concentration (fraction)



The value represents the average number of fibres in a sphere of diameter L such that when the crowding number is unity, there is just one fibre in that space. This fibre concentration [$C_v = 1.5(D/L)^2$] represents the critical concentration above which fibres are increasingly likely to collide by rotation (see picture at right). This critical concentration is very low (40-50 mg/l) so fibre collision by rotation is present throughout the papermaking system.

CSF

This is an abbreviation for Canadian Standard Freeness.

CTMP

This is an abbreviation for chemi-thermomechanical pulp or pulping process.

Curing

This term is used in papermaking to denote a chemical interaction between an additive and some part of the papermaking furnish. This interaction is normally a genuine chemical reaction, which, being temperature-driven, takes place predominantly within the drying section as part of dry end chemistry. Chemical conditions within the drying sheet may also affect the rate of cure and the use of specific additives to enhance the cure rate are termed cure promoters. Examples of such curing reactions are:

- between wet strength resin molecules to form cross-linked polymers surrounding cellulose
- between some sizing chemicals (AKD and ASA) and cellulose itself.

As the sizing of paper is a multi-stage process (even after the retention step), curing is a useful term to describe the series of stages (re-distribution, anchoring and orientation) that are necessary to size paper. Because of the temperature-dependency of the curing reactions, it is quite common for this to be incomplete at the reel. It is thus common practice to assess the ultimate cure level by artificially curing a sample of the paper at an elevated temperature for a short time, the precise conditions depending on the chemistry concerned.

Curl

This is the bending or curving of a paper sheet in one direction and is usually caused by exposure of the paper to different moisture or humidity levels. Curl can be initiated by wetting the paper on one side only, which causes the fibres on that side to swell and expand with the wetted side forming the convex (outer) surface of the curled paper. Curl can also arise when the paper is exposed to a similar moisture on both sides, but, if the paper has some two-sidedness, there may still be differential swelling/expansion leading to curl.

Cyanates

These are organic chemicals, more specifically organo-nitrogen compounds, with the $-O-C\equiv N$ group, but more important to papermaking chemicals are the iso-cyanates containing the $-N=C=O$ group and thiocyanates containing the $-S-C\equiv N$ group. Iso-cyanates are used to make polyurethanes and some thiocyanates, which are also organo-sulphur compounds, are used as biocides.

Dalton

This term is used to denote one atomic mass unit and is named after the English chemist John Dalton, who proposed the atomic theory of matter in 1803.

DBNPA

This is an abbreviation for dibromonitrilopropionamide, a commonly-used organic biocide.

DCP

This is an abbreviation for dichloropropanol.

DCS

This abbreviation is perhaps better-known in papermaking generally as standing for Distributed Control System, but, in chemical terms, it has come to stand for dissolved and colloidal substances.

DDJ

This is an abbreviation for dynamic drainage jar.

Deaeration

This is the term for the removal of air from a liquid, but a better term for papermaking is degassing or degasification as air is not the only gas (mixture) removed.

Debonder

This is the name for a chemical that reduces inter-fibre bonding by interfering with the ability of fibres to hydrogen bond with one another. . Such chemicals are mainly used in tissue grades where they also contribute to bulk and softness. Cationic surfactants are the most common type of debonding agent and are rather similar to chemical softeners. Papermaking fillers also weaken the paper structure due to interference with inter-fibre bonds, but this is not intentional, just one of several undesirable side-effects of their use as opacifying additives.

Deflaking

This is a term for a mild level of refining that is applied to some papermaking furnishes, eg those intended for tissue manufacture or using recycled pulps, where extensive refining would lead to undesirable effects on product quality (eg softness for tissue grades) and/or on machine productivity (eg water removal for recycled grades).

Defoamer

These chemicals are able to destroy an already-formed foam and, together with anti-foams and degassing chemicals, are an important component of most commercial foam control formulations. Defoamers are generally hydrophobic substances that function by one of three possible mechanisms:

- ☐ penetrating the interfacial film and interrupting the surface arrangement to produce localised weak points and ultimately bubble coalescence.
- ☐ displacing the foam-stabilising surfactant with a non-foaming surfactant
- ☐ spreading over the film surface, which produces a shearing action and subsequent film thinning.

Defoamers used by industry used to be rather simple oil-based formulations, but these have been largely replaced by more sophisticated and more cost effective water-based formulations. Oil-based defoamers were implicated in deposit problems (particularly with pitch) and losses in sizing efficiency due to the ability of the oil to dissolve the hydrophobic sizing molecule (particularly rosin). Water-based emulsion defoamers have the additional advantage that they can also be formulated with higher active contents due to having their lower viscosities than comparable oil-based defoamers.

Water-based defoamer formulations are complex and have several components:

- the liquid carrier, ie water
- the active defoaming chemical or usually a mixture of several active chemicals
- emulsifying and coupling/stabilising agents.

Water-based formulations have evolved from blends of fatty acid esters, waxes, sulphated tallow oils to include hydrophobic silicas (usually pre-treated with silicones), fatty alcohols/acids/amides and ethoxylated nonionic polymers. The particle size distribution of the emulsion particles, as well as their chemistry, is critical to their ability to interrupt the foam-stabilising film. Defoamer selection is still a matter of trial and error to some degree (albeit backed by the considerable expertise and know-how of the speciality suppliers), but the addition point should be close to where the gas is being introduced/dispersed. Chemical addition rates are around 0.5% on fibre, but this obviously depends on the "active" content of the actual product.

Degassing

In papermaking, this is a better term than deaeration as air is not the only entrained gas that could be removed, the other important one being carbon dioxide. Removal of entrained gases is one of the techniques to overcome the potential problems of foam, poor drainage and poor formation quality of the paper that may result from the entrainment of gases. Mechanical degassing through the application of a vacuum is a well-known technique (eg Ahlstrom Deculator), often applied to the thin stock to prevent drainage and formation problems, but this will not prevent foam formation in the backwater system once gases have the opportunity re-enter the liquid phase. Facilitating the natural disengagement of entrained gases is one of the three requirements (the others being some anti-foaming and defoaming activity) for a foam control additive.

Degradation

This term refers to the breakdown of a material by either a chemical reaction (eg hydrolysis) or through the agency of micro-organisms. This can take place anywhere within the papermaking system, but is most prevalent at the wet end rather than during surface application. Controlling any degradation activity is an important component within wet end chemistry.

Degree of polymerisation

This term, often abbreviated as DP, is a measure of the length of a polymer chain in terms of the number of repeating units. For example, natural cellulose in wood has a DP of about of about 10,000 glucose units, which is equivalent to a molecular mass of about 1.5M Daltons.

Degree of substitution

This term, often abbreviated DS, applies to the level of substitution in a polymer chain. It is used in two main areas in papermaking:

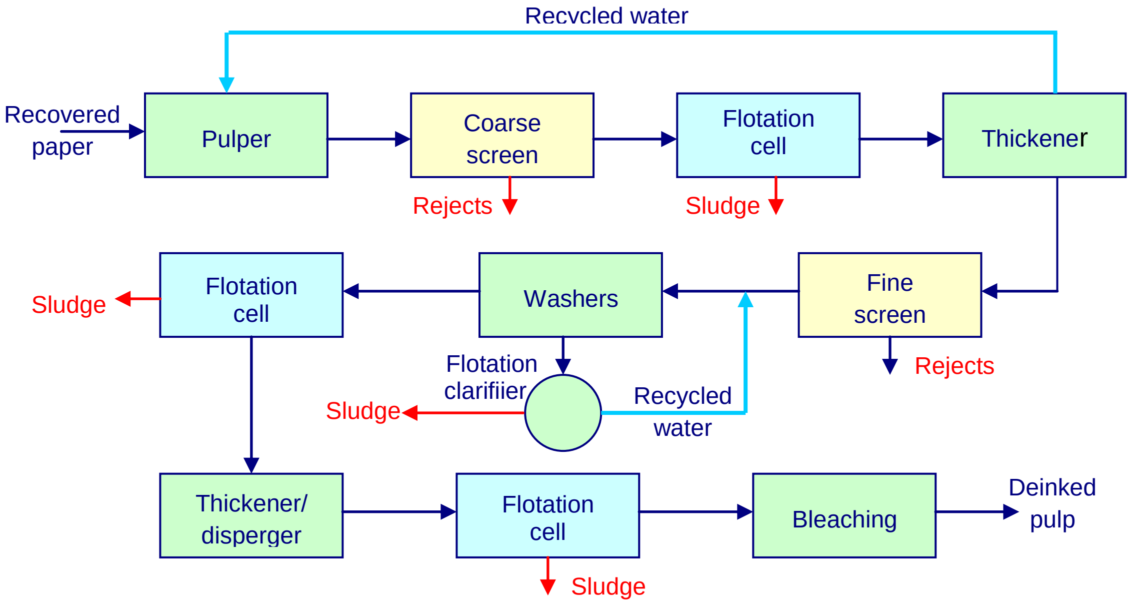
- in the case of starch or cellulose, where it refers to the proportion of hydroxyl groups that have been converted to a different form, eg to an ester or ether in the case of starches or to an anionic group in the case of carboxymethyl derivatives of cellulose. As each glucose unit has 3 hydroxyl groups, the maximum DS is 3. A DS of 0.03 thus means that 1% of the hydroxyl groups have been replaced or that, on average, there is one replacement group on one glucose unit in every 33 glucose units.
- in the case of synthetic polymers such as polyacrylamide, where it refers to the content of either anionic or cationic co-polymers and is usually expressed on a molar basis as the % charged monomer content.

Deinked pulp

This is one of the two broad categories of recycled pulp produced from recovered paper, the other being non-deinked pulp. Deinking is the process of removing from recovered paper not only any ink, but also any other constituent that is not wanted on the paper machine, eg the range of problematic substances such as stickie-forming adhesives and, on some paper machines, fillers and fibre fines. Deinking is more comparable with the mechanical rather than the chemical process for manufacturing virgin pulps and involves a series of chemi-mechanical cleaning stages, as shown in the diagram below for a typical sequence of deinking steps.

For ink removal, the two key stages are:

- flotation for removing the larger particles with chemical assistance from added soaps
- washing for removing the residual finer particles, usually with no chemical assistance, although surfactants are sometimes used.



Other chemicals used in deinking can be divided into two types:

- those added at the initial pulper stage to assist disintegration (eg sodium hydroxide) and to aid removal/suspension of inks and other dirt particles (eg sodium silicate)
- chemicals added at the final bleaching stage, which can be sub-divided into those used in the two broad categories of deinking system:
  - for wood-containing deinked grades (eg for newsprint), the bleaching agents are either sodium hydrosulphite or hydrogen peroxide, ie the same chemicals used for bleaching mechanical pulps
  - for wood-free deinked grades (eg for tissue), the bleaching agents include sodium hydrosulphite and hydrogen peroxide, but may also include FAS, oxygen and ozone. Sodium hypochlorite is a very effective bleaching agent for these grades, but is less used today than it was, mainly because of the problems associated with the chlorine-bleaching of virgin pulps.

As shown in the above circuit diagram, other deinking stages are purely mechanical and rather similar to some of the stages in the cleaning of recovered paper in non-deinking systems. The yield of recovered materials in the deinked pulp depends on the nature of the input material in relation to the desired properties of the pulp, but can be as low as 60% for tissue or printings/writings grade pulps and up to about 85% for newsprint grade pulps. By contrast, yields of 90-95% are achieved for direct-entry recovered paper used predominantly in packaging grades. The yield range from recovered paper is thus comparable with that of virgin pulp from wood.

As mentioned above, there are essentially two different types of deinked pulp:

- those made from recovered papers containing a high proportion of mechanical pulp, which are then used in somewhat similar grades of wood-containing graphical papers, mainly newsprint and, to a much lesser extent, in SC and LWC grades
- those made from recovered papers containing a high proportion of bleached chemical pulp, which are then used in various grades of wood-free paper such as tissues, towels and wood-free graphical papers.

By its nature, the deinking process has the potential to remove many of the substances present in recovered paper that could otherwise cause problems on the paper machine (see recycled pulps for a more general discussion of this). However, there are two important sets of substances in deinked pulps that can still cause problems on the paper machine:

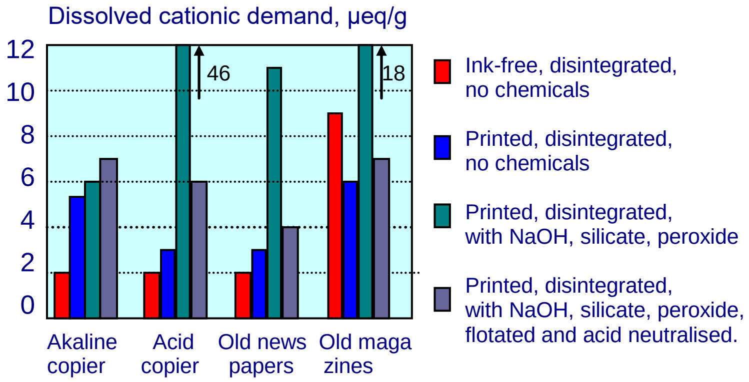
- stickies, removal of which should be one of the objectives of deinking. Potential problems on the paper machine are more related to the micro-stickies generated by mechanical action in deinking than from intact macro-stickies.
- dissolved substances, mainly the organic fraction from the recovered paper, but it can include some additives used in deinking (eg silicates). The main potential problems stemming from dissolved solids in deinked pulps are microbial activity from residual starches and impaired efficiency of cationic additives from anionic trash.

The dissolution of substances during deinking depends on many of the same factors that influence this process within papermaking, but the residual level of dissolved solids in the deinked pulp depends on the way in which water is used in deinking and the degree of closure of the deinking circuits. In an analogous way to papermaking systems, where a high degree of water closure is beneficial to the overall retention of dissolved substances in the paper, closing up of deinking circuits tends to increase the carry-over of dissolved substances to the papermaking system. However, this can be minimised by counter-current movement of process waters and by efficient thickening or washing in the later stages of the deinking process.

In the interests of a clean papermaking system, maximum dissolution during deinking is desirable, unless it can be shown that any residual water-soluble material does not dissolve under papermaking conditions, where the key variables influencing organics dissolution (pH, temperature and electrolyte levels) will probably be at different levels to those prevailing during deinking. From a yield perspective, dissolution is undesirable wherever it occurs, but it is preferable that any dissolution takes place in the deinking circuits rather than in papermaking.

It is well-known that alkaline conditions, as is normal in the first stages of deinking and during peroxide bleaching, enhance dissolution from recovered papers through their effect on fibre swelling. One reported example for a 70:30 mixture of old newspaper and old magazines indicates an increase from about 10 kg COD/tonne at neutral pH to 30-40 kg COD/tonne at doses of 2-3% NaOH on fibre. Similar increases in organics dissolution are observed when old corrugated cases are pre-treated with alkali to upgrade the strength properties of the fibres. The use of high pH to promote fibre swelling is thus a compromise between its effect in enhancing paper strength and increasing dissolution and loss of yield.

Some of the substances in virgin pulps and many of the non-fibrous additives in papermaking have some charge character and, unless they are removed during deinking, they will contribute to the charge content of the deinked pulp. Published charge data for deinked pulps is not plentiful, is often poorly characterised and is complicated by the presence of uncertain quantities of deinking chemicals (eg sodium silicate) and the (variable) efficiency of final washing. The data in the figure below shows the effect of various deinking treatments on the dissolution of charged substances (measured by titration with Polybrene). It should be noted that cationic demand of the deinked pulp passing forward to the paper machine would be much lower than the values quoted, once it has been washed and thickened. The data in the first two columns for each treatment (ie simple disintegration) are more relevant to non-deinked pulps, which are not thickened before passing to the paper machine.



Source: Kuys and Zhu in "Progress in Paper Recycling", 1997, February, 59-63.

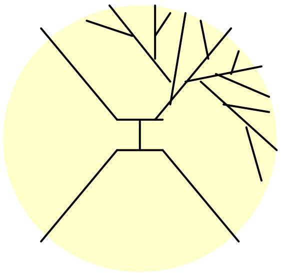
Data on dissolved charges for two other deinked pulps after disintegration give values of about 4 and 11 μeq/g. A pulp produced from deinking of office papers (see this table) contained levels of anionic substances of around 90 μeq/g by Polybrene titration of the whole deinked pulp compared to about 60-70 μeq/g using other charge titration techniques. In a more detailed study, the cationic demand of various fractions of a deinked pulp for newsprint was measured with the results in the table below. It is clear from this that the charge on the dissolved solids (0.4 meq/g) is about 10x that on the particulate solids (30 μeq/g), but the charge on the dissolved solids is partly due to concentration of recycled substances.

Parameter	Whole pulp	DDJ filtrate	Coarse filtrate	Fine filtrate
Cationic demand (µeq/l)	510	400	340	340
Suspended solids (g/l)	5.1	1.3	-	-
COD (mg/l)	-	-	870	860
Specific charge (meq/g)	0.03	0.05	0.4	0.4

An example of the influence of anionic trash in a deinked pulp is shown here for a retention aid system using colloidal silica and cationic starch. Another example is shown here for the adverse effect of residual silicate on retention aid performance. From these range of values, it is evident that the content of anionic substances in deinked pulps is somewhat variable, reflecting the wide range of input levels in raw pulps and variations in deinking efficiency.

Dendrimer

This is the name for polymers that have a highly branched structure and is derived from the word, dendra, the Greek word for tree. Because of the shape of the molecules with chains extending outwards from a central hub, they are also sometimes referred to as "starburst" molecules. This is represented by the drawing at right, where there is a similar branch-upon-branch outward chain structure on the three other spokes radiating out from the centre. A number of chemistries have been employed but, one that has been investigated as a retention aid in papermaking is a polypropyleneimine. This structure contains tertiary amine nitrogens as the branch points within the core of the molecule and primary amine nitrogens at the periphery. The cationic charge is thus dependent on pH and molecular mass, values of 13-20 meq/g having been measured for some commercial products at pH 5. The molecules are quite small with diameters in the few nm range, ie similar to nano-particles such as colloidal silica.



Laboratory investigations in Canada have been carried out on a number of mechanical pulp (TMP newsprint, SC paper) and recycled pulp furnishes and these show that the dendrimers can achieve at least comparable performance to normal polymers (such as PEI) in terms of retention and drainage at similar mass doses. They also worked well as part of a dual component system with cationic polyacrylamides and were effective for control of pitch.

Density

This is relevant to paper quality and the properties of some papermaking materials. It is normally calculated from measurements of the paper grammage and caliper:

$$\text{Paper density (g/cm}^3\text{) = grammage (g/m}^2\text{)/caliper (µm)}$$

The reciprocal density of paper is its bulk in units of cm^3/g. The density of papers varies from around 0.3 g/cm^3 (or less) for tissue grades up to about $1g/cm^3$ for heavily calendered papers. For a paper of fixed grammage, density has an important bearing on other sheet properties such as strength and porosity.

The density of filler-free paper depends on how well the fibres are able to conform to one another and on their particle size distribution. For example, mechanical treatment by refining increases density (reduces bulk) through generating fines which fill in the gaps between fibres. Pressing and calendering have the same effect simply through the applied surface pressure. Fillers increase paper density more than pulp fines as they are denser materials. The density of most fillers (clays and calcium carbonates) is about 2.6 kg/dm^3, but titanium dioxide has a density of about 4 kg/dm^3 and barium sulphate is even higher at 4.5 kg/dm^3. Plastic pigments such as those based on urea-formaldehyde are sometimes used as opacifiers because of their lower density (about 1.5 kg/dm^3).

Deposition

This term may be used in two different ways in papermaking:

- ❑ the accumulation of materials (deposits) on exposed surfaces of pipes, tanks and the paper machine
- ❑ a specific type of aggregation process where small particles (eg filler) become associated with much larger particles (eg fibre) and the small particle appears to be deposited on the larger one. This may also be referred to as hetero-coagulation.

Deposits

A deposit is any material that forms an adherent attachment to an exposed surface in process equipment, tanks and pipework. This may occur at the wet end, during paper formation (eg on wires, felts, rolls, etc) and within surface application systems. Arguably, the most widespread problems occur at the wet end, which represents a near-ideal environment for the proliferation of deposits of all types due to the high concentration of substances and a moderate-high temperature. Deposition tends to get more severe as the water system is closed up due to the concentrating effect on dissolved substances and the higher process temperatures.

Deposit-forming substances are a sub-set of problematic substances that cause a range of process and product problems, which, in the case of uncontrolled deposition, include impaired drainage, web breaks, pipe blockages, corrosion, degradation of raw materials, product disfiguration from holes and spots, etc. Deposit-forming substances can be sub-divided into two categories:

- ❑ materials already present in incoming raw materials
  - pitch originating from the extractives fraction of virgin pulps
  - white pitch from latices in coated broke
  - stickies from adhesive contaminants in recovered paper.
- ❑ deposit-forming substances generated within the papermaking system:
  - microbiological slimes of bacteria and fungi
  - hydrolysis products from additives such as AKD and ASA sizes
  - inorganic precipitates in the form of scales such as calcium sulphate and calcium carbonate
  - organic complexes between added polymers and anionic trash.

Actual deposits are a complex matrix of accumulated debris, where one set of the above materials may start the process and then act as a nucleus for deposition of other materials. These problems can be controlled using the same hierarchy of techniques summarised generally for all problematic substances and discussed elsewhere specifically for pitch and slime. In terms of non-microbiological (ie chemical) deposit problems, these are:

- ❑ selecting raw materials with the lowest possible content of deposit-forming components or their precursors

  This technique is only feasible for contaminants in virgin pulps (ie pitch), but many of these pulps (notably bleached Kraft pulps) should already include pitch content within their quality specification. For recovered paper grades, it would be good practise for all papermakers and converters to bear in mind the impacts of added materials for the recycler of their product.

- ❑ so far as it is practicable, optimising machine operation (without chemical addition) firstly to minimise deposit-forming interactions and then to minimise deposition on surfaces.

  The machine systems should be designed and constructed to maintain self-cleansing velocities in pipework, to exclude quiescent pockets and to keep tanks well-mixed. Effective showering systems on formation wires, press felts and dryer fabrics are paramount in order to prevent small accumulations of surface causing blockages and ultimately leading to stoppages and impaired product quality.

- ❑ dosing of specific control chemicals.

  There are several components within this stage of the control programme:

  - adequate monitoring of deposition to forewarn of inadequate control and to ensure that chemical addition rates are being minimised
  - system cleaning at planned machine shuts to reach the more inaccessible regions
  - continuous or semi-continuous dosing of chemicals at key locations based on either of the two main principles of modifying the contaminant particle surface to reduce its agglomeration tendency (eg detackifiers) followed by hetero-aggregation with the rest of the particulate matrix to give high single pass retention (the preferred approach) or keeping the individual deposit-forming particles apart so that cohesion into a large agglomerate is prevented (eg use of chemical dispersants). The actual chemicals used are specific to the chemical nature of the deposit.

The analysis of deposits is an obvious first step in their elimination from the papermaking system. Being potentially a complex mixture of chemical and biological components, a preliminary morphological examination under a low-powered microscope is sensible to give hints about the overall matrix in terms of fibres, fillers and bacteria/fungi. Standard microbiological techniques can be used to cultivate and identify bacterial and fungal species where necessary and the presence of certain types of activity (eg anaerobic acid production and sulphate reduction) can be confirmed by appropriate chemical analysis or simple visual assessment (eg black coloration due to iron sulphide).

For the chemical analysis, a useful initial test is dissolution under acid and alkaline conditions. This should be combined with simple visual observation such as gas evolution, which is likely to indicate the presence of calcium carbonate. Inorganic ions in the dissolved fraction can be analysed in further detail by flame emission/atomic absorption or ion chromatography. Insoluble inorganics are best analysed after combustion of the filtered residue (to remove organics) using techniques such as X-ray fluorescence. The organic matrix may not be soluble under aqueous conditions, in which case extraction with a non-aqueous solvent can be followed by any of several techniques such as infra-red, gas chromatography, etc. This microbiological and chemical detective work is often carried out by chemical suppliers as most mills do not have the required analytical facilities or expertise.

Desorption

This is the reverse process to adsorption onto the particle surface from solution and is usually undesirable. It is only applicable to substances which have previously been adsorbed at the wet end and should not be applied to the process of dissolution of water-soluble substances from pulps.

Dewatering

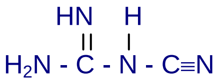
This term is sometimes used to describe the processes of water removal on the formation fabric (see drainage) and in the press section and also for the thickening of pulps.

Dichloropropanol (DCP)

This is generated as a by-product during the reaction between epichlorhydrin and an aminopolyamide to produce PAE resins. This is undesirable as DCP is classified as a possible carcinogen in some countries. DCP may also be present in CHPT, one of the chemicals used to make cationic starches.

Dicyandiamide

This chemical is an organo-nitrogen compound (formula at right) and is used as a viscosity-reducing rheology modifier in paper coatings. it can also be reacted with polyamines or formaldehyde to produce derivatives that are used as dye fixatives.



$$H_2N - \overset{\overset{HN}{\|}}{C} - \overset{\overset{H}{|}}{N} - C\equiv N$$

Dielectric constant

The dielectric constant of a substance or medium is a dimensionless parameter derived from the equation that defines the force between two electrical charges (q_1 and q_2):

$$F = q_1.q_2/\varepsilon.r^2$$

where r = separation distance and
ε is the permittivity of the medium = 8.85×10^{-12} Coulomb/Newton.m^2 for a vacuum.

The dielectric constant is the ratio of the permittivity in the medium in question compared to that in a vacuum and is sometimes called the relative permittivity. Water has one of the highest known dielectric constants (80) and this is the reason why water is such a good solvent for other polar molecules like electrolytes as the high dielectric constant reduces the strong electrostatic attractive force between oppositely-charged ions .

Diffusion

This is the process whereby molecules, in the absence of any mixing forces, migrate from a region of high concentration to one of low concentration and is a consequence of Brownian Motion. The rate of diffusion is governed by Fick's Law:

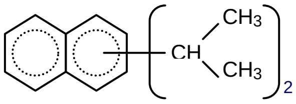
$$dm/dt = - D.A.dc/dx$$

where m = material mass, t = time, c = material concentration, x = distance in diffusion direction,
A = area and D = diffusion coefficient (length^2/time)

In most papermaking situations prior to paper formation, the papermaking stock is subject to mixing and shear forces so diffusion is not a significant process. However, in the machine's backwater system, tanks are often not mixed in any positive sense, but the contents are kept in motion by the movement of incoming and outgoing waters. Diffusion processes may be more relevant in this part of the system, particularly in dead zones and within or near deposits.

Di-isopropylnaphthalene

This organic liquid (often abbreviated DIPN) is used in the manufacture of the colour-forming capsules used in some carbonless-copy papers. The commercial product contains several isomers of DIPN (see formula at right), the proportions of the 2,6- and 2,7- isomers being particularly important.

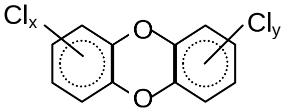


Dimensional properties of paper

The main paper properties involving its dimensions are grammage, density or bulk and sheet caliper. The dimensional stability of paper against changes in surrounding moisture is also important due to the hygroscopic nature of fibres. All fibres expand when wetted or exposed to a higher relative humidity, but the fibre diameter increases proportionately more than its length, ie the cross-direction (CD) expansion is usually greater than that in the machine-direction (MD) as most fibres are MD-aligned. This hygro-expansivity of papers can be controlled by selecting very thin fibres like esparto, by minimising fibre refining and by conditioning the formed sheet. Examples of dimensional instability in papers are curl and cockle.

Dioxins

This term is short-hand for the chlorinated dibenzo-para-dioxins (formula at right) that are sometimes labelled the most toxic chemicals in the environment. The concentration of these dioxins and the related chlorinated dibenzo-furans are usually expressed as toxic equivalents (teq) on the basis of the most toxic dioxin, the tetra-chlorinated 2,3,7,8-derivative (often abbreviated 2378-TCDD).



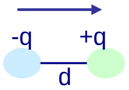
Their relevance to papermaking is that, in the mid-1980s, they were detected, albeit at very low levels, in chemical pulps that had been bleached with chlorine. This led to an enormous research programme by the industry to find the source and cause for this and then to modify existing practices to eliminate their presence. This has been very successful to the extent that, despite advances in dioxin analysis, dioxins (or furans) cannot be detected in pulps or waste streams from chemical pulp bleaching plants that have adapted their processes in the appropriate way. Essentially, this has meant moving away from reliance on chlorine as the principle chemical agent for lignin removal in favour of chlorine dioxide and non-chlorine containing agents such as oxygen, ozone and hydrogen peroxide.

DIPN

This abbreviation stands for di-isopropyl-naphthalene.

Dipole moment

This concept applies to situations where there are two opposite charges (as shown at right), the dipole moment being defined as:



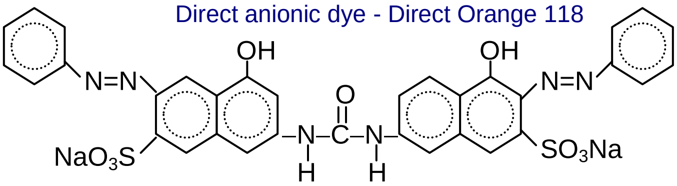
$$\text{dipole moment (Coulomb}^2\text{.metre)} = q^2/d$$

The alternative unit is the Debye where 1 Debye = 3.34×10^{-30} C^2.m. Any molecule that has a negatively-charged area (or ion) separated from a positively-charged area (or ion) has a permanent dipole moment and is said to be polar. The direction of the dipole moment is towards the positively charged entity. Molecules with a dipole moment align themselves in an applied electric field. Substances without a permanent dipole moment can have an induced dipole moment when placed in an electric field and are then said to be polarised. A substance's dipole moment and its polarisability are two of the important factors in terms of the attractive van der Waals forces that exist between all substances and are also important in relation to a substance's dielectric constant.

Direct dye

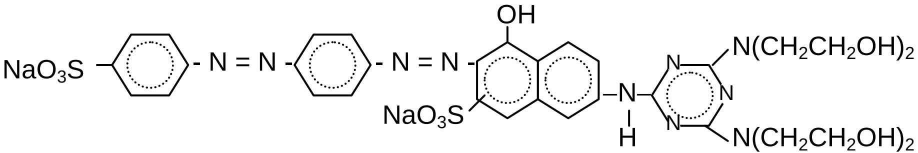
As their name suggests, direct dyes were developed to have better adsorption on and affinity for the particulate surface than traditional dyes. For both anionic and cationic direct dyes, this is achieved by having larger and more planar molecules so that the dye can get closer to the particulate surface. Direct dyes are thus more substantive (than non-direct dyes) to bleached chemical pulps and have good fastness characteristics. Because of these desirable attributes, direct dyes are now the most common type of dye used in papermaking for both wet end and surface application. For reasons of chemical compatibility, anionic direct dyes are preferred for surface applications, whereas the cationic direct dyes usually show the best performance at the wet end.

Direct anionic dye - Direct Orange 118



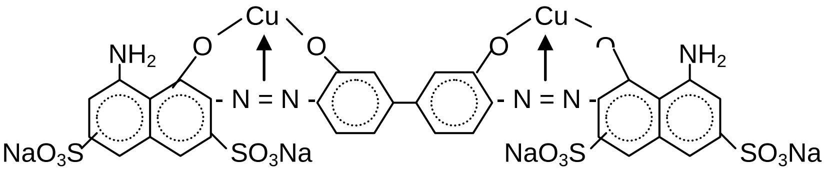
An example of a direct anionic dye is Direct Orange 118 as shown at right. It is evident that these dyes have some resemblance to the traditional acid dyes, but the molecules are significantly larger. Water solubility and the anionic character are due to the sulphonate groups, whilst the colour is due to the extensive, delocalised π-electron system involving two azo groups. Despite their better substantivity, their anionic character means their efficiency is still improved markedly by the presence of hardness salts or through the use of alum or fixatives.

Direct Red 253 (formula below) is made by modifying a simpler dye (Direct Red 81) to introduce more hydroxyl groups, which give better substantivity through hydrogen bonding with the fibre. The introduction of hydrophilic groups (such as hydroxyl) requires care as this can make the molecule too water-soluble, which would impair substantivity.



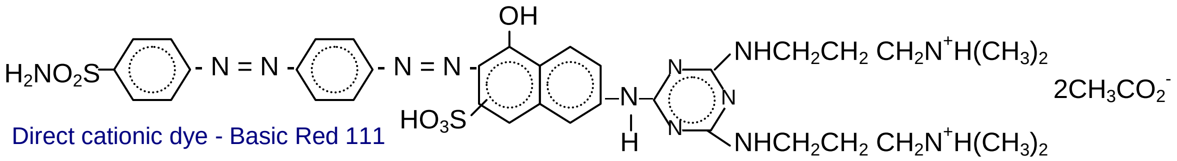
Direct anionic dve - Direct Red 253

Some anionic direct dyes utilise metal ions (eg copper) to improve fastness properties. This is shown below for a blue dye, where the planarity of the molecule is helped by the co-ordinate link from the azo groups to the copper (II) ions.



Direct anionic metal complex dye - Direct Blue 261

The cationic direct dyes are the most substantive as they combine a positive charge with a large, linear, planar molecule. This is shown below for a red dye, where the tertiary nitrogen on the substituted amine group gives excellent adsorption on fibre.



Direct cationic dye - Basic Red 111

The overall adsorption of direct dyes includes most of the possible mechanisms for dyes generally and these are discussed in more detail under dyes.

Disinfection

Disinfection is the process of achieving sterility (freedom from micro-organisms) in a material or location and is only used in papermaking in terms of one raw material, fresh water.

Dispersant

This is a type of chemical used to stabilise suspensions of colloidal particles (ie to produce a dispersion). Dispersants are able to do this by adsorbing on particle surfaces and preventing aggregation through either electrostatic repulsion or steric stabilisation. They are used in papermaking for several applications:

- to prepare stable dispersions of AKD and rosin sizes and emulsions of ASA size
- to stop some wet end materials and micro-organisms forming deposits
- to allow fillers or pigments to be supplied in a slurry form at high solids content without aggregating together prior to use at the mill
- to maintain coating solids in a finely-divided state.

In the case of deposit prevention, dispersants can be used in their own right or be part of formulated commercial products, eg biocides. Enzymes can be considered to be a type of dispersant that is used to stop micro-organisms forming slimes. Some dispersants (notably anionic substances) can cause problems in wet end chemistry through their ability to neutralise cationic additives. The main source of this problem is dispersants (eg polyacrylates) used in filler and pigment slurries.

Dispersion

A dispersion is a uniform distribution of one material in another and is most commonly applied to colloidal systems. The most common sort of dispersion in papermaking is a suspension of particulate materials in water. As many particles have some tendency to aggregate together (particularly when not being positively mixed), it is often necessary to use chemical dispersants to stabilise the suspension in a fully dispersed state.

In wet end chemistry, dispersion is generally an undesirable process, which would tend to lower single pass retentions, but dispersant chemicals are still sometimes used in relation to deposit control. However, dispersion is an important process within paper coating where the particulate components must be prevented from aggregation in order to produce a uniform coating layer. AKD and rosin sizes are also dispersions (not emulsions as they are both solids), but, as they are quite strongly hydrophobic, they require a dispersing agent (cationic starch for AKDs and often the protein, casein, for rosin) to stabilise them in an aqueous system.

Dissolution

This term means simply putting a substance into the form of a solution, which, in papermaking terms, means in aqueous (water) solution. Many raw materials are supplied to the mill in a dissolved form for ease of application (wet strength resins, dyes, brighteners, etc) and others are deliberately dissolved in water before addition to the papermaking system (eg starches). In this document, the term "dissolution" is applied to substances that are not deliberately dissolved in water, but which dissolve incidentally from a particulate state (eg from pulps) simply because they are water-soluble. An alternative term for this type of dissolution is leaching or extraction from the particulate material.

Dissolution is mainly relevant to wet end chemistry, but it can also occur when a base paper passes through a surface applicator such as a size press. In both cases, dissolution is undesirable as it is likely to cause problems, eg at the size press, the substances dissolved from the paper web might interact with chemicals in the size press solution causing precipitation and perhaps deposition elsewhere in the size press circuit. Dissolution at the wet end can be broken down into two sets of substances:

- ☐ organics originating from pulps such as
  - hemi-celluloses from virgin pulps
  - starches from size press-treated broke and recovered paper
  - coating dispersants from coated broke.
- ☐ inorganics such as:
  - calcium carbonate when exposed to acidic conditions
  - neutral electrolytes from virgin and recycled pulps.

As is evident from this list, the dominant source of such materials is pulps and the dominant type of material dissolved on most paper machines is organic. The highest levels originate from machine broke that has been surface-treated and from recycled pulps that are not deinked beforehand. In these cases, substances that dissolve readily at the wet end could account for 5% or more of the pulp, most of this material being starches. However, high levels of inorganic electrolytes can be generated by dissolution, not so much from pulps but rather by dissolution of calcium carbonate when microbial activity is not well controlled. In fact, the highest level of dissolution of both sets of substances tends to occur on recycled liner/fluting machines operating substantially- or fully-closed water systems.

On most paper machines, the solids dissolved in this way account for most of the total dissolved solids at the wet end (see baseline chemistry for some examples of this). As the single pass retention of all dissolved substances never exceeds about 2%, they build up rapidly in the papermaking circuits, particularly on machines with closed water systems (see this example). Most (if not all) substances that dissolve in this way are problematic substances that are responsible for undesirable effects such as slime growth, chemical deposits, foam, chemical interference, etc. One of the important management issues within wet end chemistry is thus to minimise dissolution.

Some of the factors affecting dissolution are discussed under solubility. Examples of dissolution of organics are given in the sections on bleached Kraft pulps, bleached mechanical pulps, chemimechanical pulps, ECF pulps, non-deinked recycled pulps and TCF pulps. At the extreme, the total dissolved solids present at the wet end can reach levels of about 50 g/l, nearly all of which comes from dissolution. These very high concentrations occur on machines making recycled liner/fluting, where the water systems are completely closed (see this table for machine data). As most of the substances dissolving in this way are organics, this aspect is discussed further under dissolved organics.

Dissolved organic carbon

This parameter is more widely used for wastewater monitoring, but is occasionally utilised as an alternative to COD for wet end monitoring of dissolved organics. The measurement is often referred to (incorrectly) as total organic carbon (TOC), but, as most analysers cannot deal with particulate solids, the measurement is more accurately termed dissolved organic carbon. Inorganic carbon from bicarbonates is normally removed prior to organic carbon analysis by acidification and gas stripping. For carbohydrates, the carbon content is about 44% of the mass or about 37% of the COD. The DOC:COD ratio gives information about the carbon's "state of oxidation", ie organic compounds are somewhere between the 1:0 ratio for carbon dioxide and the 1:6 ratio for methane (CH_4) with starch being about 1:2.7.

All DOC analysers are based on conversion of organic carbon to carbon dioxide, but differ in terms of the method of carrying out this conversion and the method of measuring the amount of released CO_2. There are two conventional conversion methods, but most modern analysers use photochemical oxidation with UV light instead of the more traditional high temperature combustion. Oxidising chemicals (eg persulphate) are sometimes added during photo-oxidation to improve conversion efficiency. Three methods of measuring the released CO_2 are in commercial use:

- ❑ direct measurement in the gas phase using an infra red detector
- ❑ reduction of CO_2 to methane which is then measured by a flame ionisation detector
- ❑ indirect measurement of the CO_2 by conductivity after dissolution in water.

In terms of DOC analysis at the wet end, research has shown that DOC can be a useful surrogate parameter for cationic demand, but this is true only if the anionic fraction of the dissolved organics remains reasonably constant. DOC measurement in the laboratory is easily adapted to on-line measurement sensor as the laboratory unit is fully automated apart from sample loading. The ABB WIC on-line monitoring system can incorporate a DOC analyser. Some DOC concentrations are quoted here for several machines with fully-closed water systems.

Dissolved organics

In wet end chemistry, the set of dissolved organic substances is one of the two fractions within the total dissolved solids, the other fraction being the dissolved inorganics or electrolytes. The materials added at the size press are nearly all dissolved organics (eg starches), but their dissolved character tends to be taken for granted. In normal aqueous coating, the dissolved fraction is relatively minor compared to the particulates and is largely organic in nature. At the wet end, the levels of dissolved organics are usually measured either via their oxygen demand (as chemical oxygen demand) or their carbon content (as dissolved organic carbon). COD is the most common technique.

There are three possible sources of dissolved organics at the wet end:

- ❑ those taken in with the fresh water, but this can normally be neglected as insignificant, so the baseline concentration is close to zero
- ❑ those derived from other raw materials which can be further sub-divided into:
  - chemicals added in a solution form to the wet end, eg starches, wet strength resins, etc, but this contribution should be low as these chemicals are primarily selected on the basis of their high adsorption on the particulate matrix
  - substances which are added to the wet end associated with a largely particulate set of materials (pulps, including broke), but which then dissolve in the liquid phase.

The dominant source is thus dissolution, which is quite a complex process for organics because of the enormous variation in their chemistry and in their molecular size. Most organics dissolving from pulps are polymers, although there are a few exceptions to this such as fluorescent brighteners in the case of dissolution from some recycled pulps and broke. As most polymers present are hydrophilic, their inherent solubility is not likely to affect the extent of wet end dissolution at the normal levels present.

For chemicals that have been added to paper by surface application, their dissolution from broke or from a recycled pulp is relatively easy if they are inherently water-soluble (eg starches and brighteners). An example is given here of the dissolution of organics from various grades of recovered paper. If the chemical has a charge attraction for the particulate surface (eg size press cationic starch), it will be held in an adsorbed state and this is one of the advantages of using such chemicals for surface application.

For the organics that are present in virgin pulps (eg hemi-celluloses), the situation is somewhat different as they may be located inside the fibre wall and thus have to diffuse through the fibre wall before they reach the external water. Unless the polymer is small enough to diffuse through the pores within the fibre wall, it cannot dissolve in the bulk water so the critical factor is the size of the polymer versus the size of the pores (see discussion under accessibility). The factors that influence the conformation and size of polymers are discussed under polymers and the size of the pores in the fibre wall is discussed under swelling.

In addition to the loss of yield and increased wastewater losses, the dissolution of organics at the wet end also has two major undesirable effects depending on the chemistry of the substances concerned:

- biodegradable organics such as starches from broke and recycled pulps make a substantive contribution to wet end microbiological problems
- charged organics such as anionic hemi-celluoses from virgin pulps and dispersants from coated broke and coated recovered papers contribute to anionic trash.

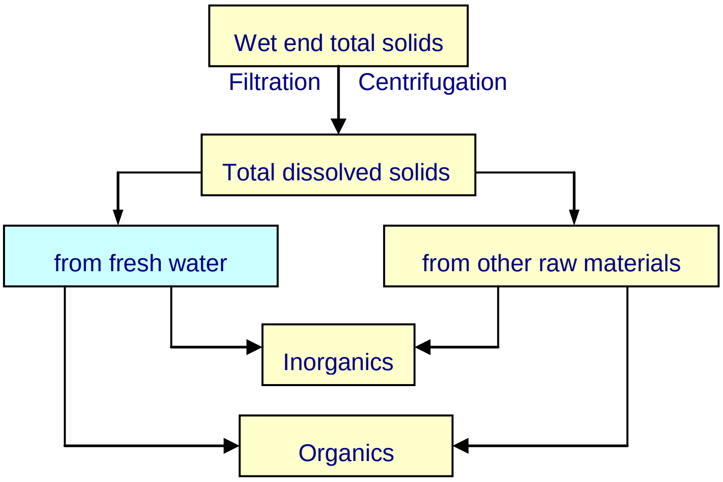
Uncharged (nonionic) dissolved organics such as native starches could in principle stabilise fine particles through a steric stabilisation mechanism, but it is generally considered that the wet end concentrations are not high enough. The exception to this might be 100% recycled machines making packaging grades which tend to run with substantially or even fully closed water systems. The concentrations of dissolved organics on such machines can be up to around 30 g/l (as COD), but, as this is composed mainly of starches, they are very degraded and this would limit their ability to act as protective colloids. At the other end of the spectrum, machines running with virgin pulps and no/little starch addition have concentrations of dissolved organics measured in 100s mg/l (as COD) and there are a lot of machines operating with intermediate COD levels of 1-3 g/l.

Examples of COD levels on different paper machines are shown here for a recycled wet strength towel and here for a coated wood-free machine. For any particular paper machine with a consistent raw material input, the concentration of dissolved organics is determined by the degree of water closure and a typical profile for the build-up of dissolved organics on closing up is shown here. Levels of dissolved organics (as COD or DOC) are quoted here for several machines with fully-closed water systems. When considering the effect of closing up on the levels of dissolved organics at the wet end, the influence of electrolyte levels and temperature must always be borne in mind and, as these also change on closing up, there can be complex feedback effects as discussed further under water closure.

Dissolved substances

These substances are sometimes referred to as "dissolved and colloidal" substances or materials (often abbreviated DCS or DCM). The reason for this is that, when particulate materials are removed (by either filtration or centrifugation) from a wet end sample (stock or whitewater), the liquid phase fraction often contains colloidally-dispersed solids as well as molecularly-dispersed (ie genuine soluble) solids. In this document, they will be referred to simply as dissolved substances.

Dissolved substances at the wet end play an important role in wet end chemistry, but less so in product chemistry as, except on paper machines approaching full water closure, they are not well retained in the paper due to their very low single pass retention. Materials applied at the size press are normally present as dissolved substances, but the majority of materials applied in normal aqueous coating are in a dispersed particulate form.



The dissolved substances present at the wet end of paper machines can be categorised in various ways (see summary diagram above), but a useful initial sub-division is into two fractions depending on their source rather than on their chemical nature:

- those taken in with the fresh water, which are mainly inorganic electrolytes
- those derived from other raw materials which can be further sub-divided into:
  - chemicals added in a solution form to the wet end, eg starches, dyes, etc, which are intended to be largely adsorbed by the particulate matrix and thereby retained in the paper
  - substances which are added to the wet end associated with a largely particulate set of materials (pulps, broke and calcium carbonate), but which then dissolve in the liquid phase.

This distinction as to the source of dissolved solids is important as those derived from fresh water do not build up as the machine water system is closed up. The fresh water chemistry establishes what might be called the baseline chemistry and other raw materials contribute to this depending on their input load and single pass retention.

The important characteristics of the dissolved solids are:

- pH and the associated acidity or alkalinity
- the content of dissolved inorganics (electrolytes which are normally measured as conductivity) and the concentration of specific ions within that fraction
- the content of dissolved organics (measured as COD or DOC) and the concentration of individual organic compounds
- the content of charged substances (measured as a charge demand by titration with oppositely-charged polymers). These materials are normally a sub-set of the dissolved organics as electrolytes are not measured in the techniques used to quantify charge demand.

Disturbing substances

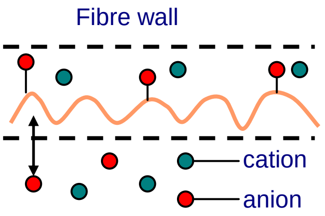
This is an alternative name for interfering substances.

DOC

This is an alternative name for dissolved organic carbon.

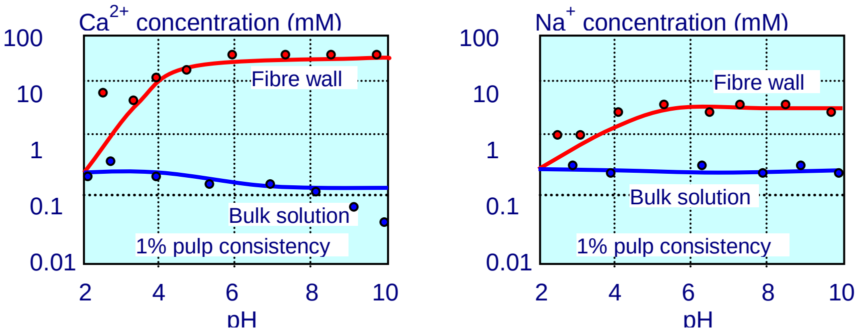
Donnan effect

The theory behind this effect was developed to explain the unequal distribution of ions on each side of a membrane, where one ion is restricted to one side because of its large size. It was later applied to more general situations where one ion or ion type was localised within one part of a system and it has since been applied to papermaking pulps in terms of the difference in ionic concentrations inside and outside the fibre wall. This is illustrated in the simple picture at right, which shows an anionic hemi-cellulose, which is too large to be able to squeeze through the pores in the fibre wall and the mobile cations/anions that can move freely through the fibre wall. The ability of such hemi-celluloses to reach the bulk solution depends on their size relative to the size of the holes (pores) in the fibre wall (see also discussion under accessibility), which depends on the degree of fibre swelling.



The Donnan theory states that, when both diffusible and non-diffusible ionic substances are present, there will be a higher equilibrium concentration of diffusible ions on the side containing the non-diffusible charged substances, ie in the case of a pulp suspension, there will be a higher cation concentration within the fibre wall than in the bulk solution. As the ionisation of the anionic hemi-celluloses increases with pH (see this example for the pulp zeta potential), the difference in cation concentrations across the fibre wall should also increase with pH.

This has been verified experimentally as shown below for one unbleached softwood Kraft pulp, where the sample was taken directly from the pulp mill. This pulp had an anionic group content of 85 µeq/g and a fibre saturation point of 1.4 g water/g pulp. The ratio of the ion concentrations inside and outside the fibre wall is about 10x for sodium and 100x for calcium. Obviously, the mass distribution of ions depends on the pulp consistency (ie on the ratio of water in the fibre wall to bulk water), but, at the 1% pulp consistency used in this study, there was about the same amount of calcium ion in the fibre wall as in the bulk solution. This concept is very important to the form of the pulp's anionic groups in papermaking, where the pulp encounters a different set of cation concentrations than at the pulp mill and a process of ion exchange takes place to establish a new equilibrium.



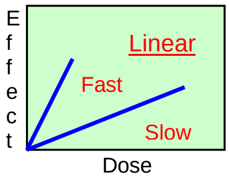
Source: Towers and Scallan J.Pulp Paper science, 1996, 22, 9, 332-337.

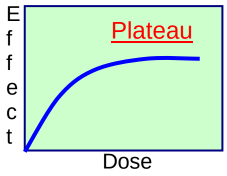
Dose-response effects

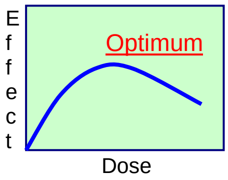
In papermaking, the response to the addition of a wet end chemical depends on several factors:

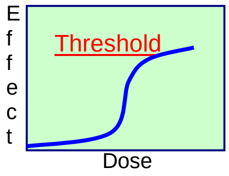
- the initial retention of the chemical in the sheet
- the positioning of the chemical within the sheet structure
- the ability of the chemical to express its inherent functionality, which may depend on factors such as the temperature profile in the drying section.

Many different dose-response relationships for papermaking materials are possible as shown by the few examples here. An ideal paper chemical would have a predictable linear effect (as shown at right) with a fast response, at least when the dose is plotted as cost, rather than mass, per tonne of paper. This type of response is achievable by, for example, fillers in relation to paper opacity, but only if their retention (and state of aggregation) remains constant as the dose is increased.









If filler retention drops off at high doses, then the response curve would become more like that in (B). However, this second declining/plateau response pattern is most common for those papermaking additives whose single pass retention relies on initial adsorption onto the particulate matrix, eg the normal dry strength and wet strength aids, polymer retention aids, etc. This effect is due to the available surfaces becoming eventually saturated with adsorbed material, so that addition beyond a certain dose is effectively pouring the chemical down the drain. The only way to adsorb more chemical is to increase the surface area or some other relevant parameter such as surface charge.

The optimum dose curve is quite common for chemicals like cationic retention polymers, where an excessive polymer dose simply re-stabilises the particle with the opposite charge and retention drops. Cationic additives of any type do not always work as quickly as intended and sometimes their response curve is delayed due to some threshold effect. This is the classical effect caused by the presence of anionic trash, which ties up the cationic additive before it can interact with the particulate surface. This response pattern is not limited to soluble additives as it is also the sort of response pattern when sizing chemicals are used. In this case, it is due to the fact that adequate sizing is not achieved until all the particulate surfaces have been adequately covered with hydrophobic material.

Dosing

The vast majority of papermaking chemicals are added to the system in a liquid form, largely on the grounds of ease of automated dosing. Even chemicals that are natural powders (eg mineral fillers) are increasingly being supplied in this form (in this case as a slurry) even when this involves the need to incorporate chemical auxiliaries (eg dispersants) that can cause problems. There are some exceptions to this (eg talc addition for pitch control), but, on most paper machines, pulp is the only raw material added in a dry form. This comment applies equally to all three major chemical addition systems - the wet end and, where present, the size press and coater.

In addition to knowledge about the dose-response relationship for the additive, there are (at least) four important issues in dosing:

- to control the dose at the required level

  This has been assisted considerably over the last 20 years by developments in on-line monitoring sensors, which allow the dose to be controlled by a feedback signal from the sensor(s) and associated data handling system. However, manual set points on dosing pumps still have to be used for many additives, where sensors are still lacking (eg dry and wet strength).

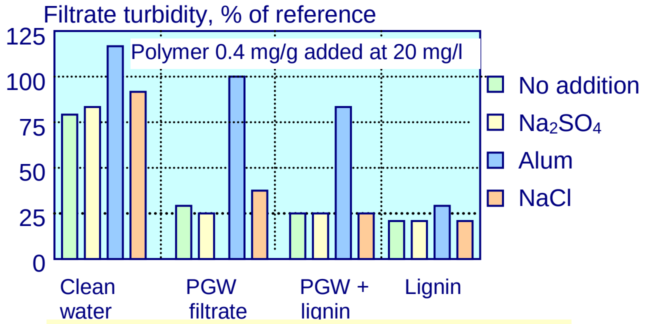
- to dose the chemical at the optimum position in relation to other additives

  This is critical for some additives and less so for others. There are several different reasons why the efficacy of additives depends on the order of addition such as competitive adsorption effects, collision frequencies between particulate solids and charge-mediated interactions between additives (eg between fluorescent brighteners and cationic polymers).

- to mix the chemical into the body of water as rapidly and uniformly as possible.

  Poor mixing at the point of addition leads to localised interactions between the additive and the stock and poor distribution. The most uniform distribution is usually achieved at high shear for a short duration. Many papermaking chemicals (eg sizes) are dosed into the papermaking stock at the supplied solids content with no pre-dilution. However, some additives (notably some polymer solutions) are pre-diluted in order to lower their viscosity and facilitate uniform mixing. This can involve quite significant quantities of water and normally fresh water is used.

  In relation to polyacrylamides (one of the most common types of retention chemical), research has shown that recycled water can be used for dilution, but that anionic substances in the water can reduce its efficacy. This is shown in the figure at right using a PGW pulp where waters of four different qualities were used to dilute the cationic polyacrylamide from 2 g/l to the working concentration of 20 mg/l. (In this figure, lower turbidity values indicate impaired retention aid efficacy).



Source: Ryoso in Appita J., 2001, 54, 1, 22-26.

  As in the case of interactions with anionic trash when a polymer reaches the paper machine system, these effects are not stoichiometric as the charge in each of the three sets of samples was the same at about 80 μeq/l, but the adverse effects were slightly different. The electrolyte effects were quite small, except for the alum, which improved the efficiency due to its ability to neutralise the anionic trash. Recent developments in dosing arrangements (such as the Finnish TrumpJet system) have shown that its is possible to use recycled waters for dilution of not just retention chemicals, but also of biocides, dyes, sizing agents and cationic starch. In one application with ASA size, such an approach has reduced the standard deviation of the paper's Cobb value by about one third.

- ❑ to provide the optimum shear and contact time before sheet formation or surface application. Prolonged high shear can be deleterious, notably for the state of aggregation of the wet end stock and for the distribution of adsorbed additives. At the wet end, there is a choice between adding chemicals to the thick stock system (with lower shear levels and longer contact times) or to the thin stock (with higher shear and shorter contact times). There are several examples in this document of the effect of shear level/duration on flocculation - see here for polyacrylamide, here for polyacrylamide/polyethyleneimine, here for polyacrylamide/bentonite and here for colloidal silica with cationic starch or polyacrylamide.

The above points are relevant to wet end addition more than surface application as the latter are always mixed together prior to pumping to the applicator.

DP

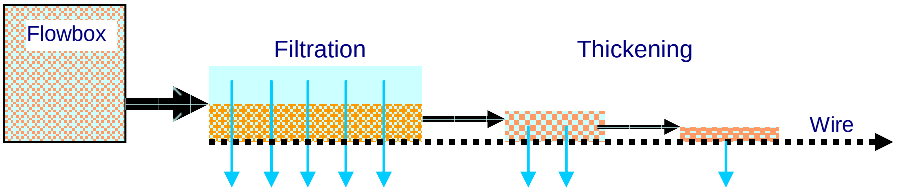
This is an abbreviation for degree of polymerisation.

Drainage

This is the process of water removal from the papermaking stock in the initial paper forming (wire) section. This is important in terms of:

- ❑ minimising energy consumption during later pressing and final drying
- ❑ maximising the strength of the wet web in order to improve runnability and minimise sheet breaks, particularly through the press section.
- ❑ defining the lowest practicable flowbox consistency in order to maximise the formation quality of the paper at the desired machine output
- ❑ determining the losses of particulate solids from the wire part and hence the wire retention.

The development of new types of paper former means that water is now removed from the stock in several different ways, but there are still two basic water removal mechanisms - thickening and filtration (see summary in diagram below). On most paper machines, the movement of water is in one direction only, initially by gravity alone with assistance from stationary devices (table rolls or foils) and then with further assistance from the application of vacuum. An initial forming board slows down the initial drainage rate so that excessive fines are not lost and the sheet is not sealed, which would slow down later drainage. High initial drainage by filtration also leads to some sheet two-sidedness. Foils or rolls provide upward pressure pulses to give some re-distribution of sheet components for good formation and downward pulses for good drainage. Strong pulses have an adverse effect on wire retention. The design and set-up of the formation wire and its auxiliary elements thus play a key role in stock drainage and the formation quality of the sheet.



This initial filtration stage of water removal removes the “free” (unbound) water loosely held within the larger web interstices and increases the consistency from 1-10 g/l (0.1-1%) at the flowbox to 3-5% depending on the grade being made. The hydraulic loading on the formation wire varies in the range 10-100 litre/m^2 (depending on initial consistency, grammage and retention), which gives an application depth of 10-100 mm on the formation wire. Once the mat consistency reaches the few per cent level (at about the vacuum boxes), most of the solids are immobilised and subsequent water removal is by thickening. At the end of a normal Fourdrinier table, the consistency has increased to 15-22% and at least 96% of the water has been removed by this combination of filtration and thickening.

With other formers, the drainage pattern is more complex. On machines with top wire drainage units, some water is removed from the top-side from about half-way down the table; this results in some impairment of retention. On gap formers, drainage takes place in both directions right from the flowbox producing a well-formed sheet, but with relatively poor retention. Board machines utilise a wide variety of former types from traditional cylinder moulds to Fourdrinier sections, but generally have high retentions and slow drainage in the later stages of water removal due to the high sheet grammage.

Drainage through a porous medium such as a fibrous mat can be modelled in various ways such as the following version of Darcy’s Law for laminar flow situations:

drainage rate (volume/time.area) = $\Delta p/\eta R$

where Δp = pressure gradient across mat/wire = pressure difference/depth,
η = filtrate viscosity and R = total resistance to water passage of mat and wire.

It should be noted that the drainage rate is dependent not only on the characteristics of the applied suspension, but also on the formation fabric (wire) in terms of its design and its state of cleanliness. The design of formation fabrics is an important subject in its own right and cannot be dealt with in any great depth here. The common term "wire" for formation fabrics goes back to the time when bronze was the most common material of construction, but formation fabrics are currently made of polyester filaments. These are combined together to give different weft/wove and layer characteristics, which determines the fabric's permeability. Forming fabrics are selected on the basis of their longevity and the required combination of drainage, retention and formation qualities. The drainage properties of the wire would deteriorate quite rapidly with time due to the accumulation of debris from the stock and possible microbiological growth, so cleaning with water is a critical part of their overall management.

In terms of the papermaking stock, drainage increases with temperature (due to the consequent decrease in the viscosity of water), so drainage improves as water systems are closed up due to the associated rise in temperature (see this figure). Steam boxes are sometimes used on the papermaking wire to enhance sheet temperature (without having to use high energy inputs to heat the whole stock) and thus improve water removal during later pressing. The overall resistance to filtration of the stock can be handled using the Kozeny-Carman equation, which shows that, for particular set of component materials at a particular grammage, it is dependent on their void volume and surface area, which determines their permeability. Overall, drainage depends on a number of physical and chemical characteristics of the stock:

❑ the particle size distribution of the papermaking stock

This is important for its direct impact on mat permeability and is influenced by many factors such as the blend of pulps, their freeness (which determines the level of pulp-derived fines) and the amount of any filler added. The retention of unflocculated fine particles by filtration leads to their accumulation on the top-side and to partial sealing of the web, which impedes drainage.

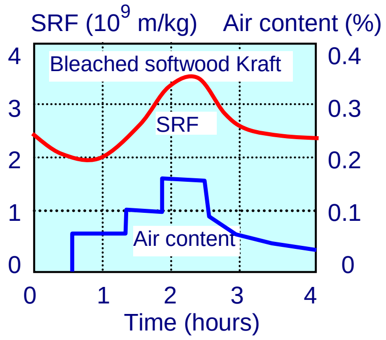
Aggregation of the fine particles facilitates the passage of water and is accomplished through the addition of conventional drainage aids.

- the chemistry of particle surfaces

  This is important in relation to the particle's ability to hold on to water, which depends on their hydrophile:lipophile balance (HLB). Most papermaking materials (like cellulose and fillers with adsorbed starch) are very hydrophilic and can hold on to water through hydrogen bonding. This is quite difficult to negate, but is possible by the use of a newer form of drainage aid, cellulase enzymes. Fillers themselves tend to aid drainage due to their lack of hydrogen-bonding ability, but their shape is also important with the more regular-shaped fillers (such as natural calcium carbonates) allowing more rapid drainage than platy fillers (such as clays).

- the entrained gas content of the stock

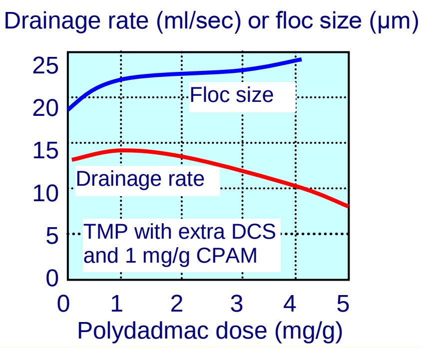
  This is undesirable for many reasons, but it can impede water removal, particularly during the later vacuum-assisted stage as the applied vacuum will tend preferentially to remove the gas rather than water. Also, any consequent bubble-filled holes in the paper web allows the early loss of vacuum at the paper surface thus reducing the duration of full vacuum. An example of this is shown at right using a laboratory drainage analyser in terms of the impact on the pulp's specific resistance to filtration (SRF).



Source: Karras, M in Tappi J., 1989, February, 155-159.

The freeness of the papermaking stock is an important control parameter on most paper machines, but this is mainly used as a means of controlling the level of pulp refining rather than drainage itself. Nevertheless, most paper machines thus have information on drainage characteristics, usually from off-line freeness measurement, but increasingly via on-line freeness sensors (such as that from BTG). On-line assessment of drainage is usually done by measuring the time taken to collect a specific volume of filtrate or the volume draining in a specific time. Many researchers and others working in this area have developed their own laboratory drainage analysers so that comparative tests can be carried out (except that the sheer number of different devices can make comparisons between different studies virtually impossible). These analysers often bear some resemblance to the dynamic drainage jar used for laboratory retention tests and are frequently referred to as dynamic drainage analysers. They do differ in one important respect from a DDJ in that a mat of paper is allowed to form and also a vacuum may be applied to simulate actual conditions on a papermaking wire.

A set of results from one such analyser is shown at right for a TMP furnish with added dissolved and colloidal substances (DCS). The drainage rate is the volume of drained water divided by the overall time until the vacuum is lost, which occurred when the mat was about 10% solids content in all cases. The drainage rate of the TMP stock was about 11 ml/sec and this increased to 22 ml/sec with only the cationic polyacrylamide (CPAM), but no extra DCS. In this particular example, the drainage shows an optimum polydadmac dose of about 1.5 mg/g pulp, but this not clearly related to an optimum floc size.



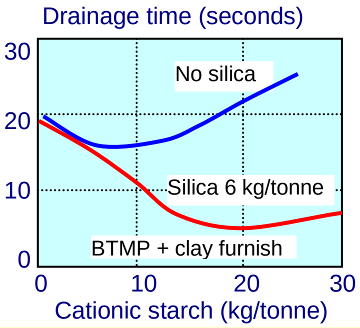
Source: Dunham, A et al in J. Pulp Paper Science, 2002, 28, 9, 298-304.

Drainage aids

These are chemicals added to the papermaking stock to improve the rate of water removal, notably of drainage on the formation wire, but also possibly during pressing. Improved water removal can be harnessed in one of two ways:

- by increasing the production rate (machine speed) through being able to pass more paper (at a lower moisture content) through the press and/or drying sections. A secondary benefit of this is the higher wet web strength and thus better runnability.
- by maintaining the same production rate, but forming the paper at a lower flowbox consistency in the interests of improving the paper's formation quality.

The most common mechanism for drainage improvement is aggregation of the fines, which otherwise impede the passage of water at the paper surface and through the web interstices. This best type of aggregation for drainage improvement is either through the patch mechanism with single polymers or the more complex network aggregation with micro-particle dual chemical systems. An example of drainage improvement with colloidal silica is shown at right for a model SC paper furnish (mainly bleached TMP plus clay filler) in a laboratory drainage analyser. The adverse effect of high cationic starch doses on drainage in evident, but the silica addition (albeit at a rather high dose) improves drainage at all starch levels.



Source: Persson et al in Paper presented at SPCI Conference, Stockholm, 1996.

Single patch-type polymers and micro-particle systems both give small, dense particulate aggregates, which drain reasonably and respond well to vacuum-assisted drainage, but single polymer drainage aids are not as effective at raising retention as bridging polymers. Even though the solids content of a compact-floc system may be worse than that of large-floc system before the vacuum boxes, it will usually be higher at the couch. The objective behind the addition of drainage (and retention) aids is to increase aggregation of the fines without unacceptable aggregation of the fibres (see this figure for illustration). Shear levels play a very important role in the performance of such chemicals and this is discussed further under that heading.

A rather different approach to drainage improvement is provided by enzymes. These are usually cellulase enzymes, although combinations with "hemi-cellulases" (enzymes able to break down hemi-celluloses) have also been tried. The main areas of application have been on recycled furnishes and on poorly-draining virgin pulp furnishes such as for the manufacture of release papers and NSSC-based fluting. The mechanism is believed to involve removal (dissolution) of some of the more water-retentive parts of the pulp fibre/fines by a "peeling" action, the disadvantage of this being an increase in dissolved organics and some loss of overall pulp retention/yield. However, the potential advantage of enzymes for drainage improvement is that this is achieved without changing the state of particle aggregation, as would occur if chemical drainage aids were used. Aggregating chemicals can still be used to optimise particulate single pass retention, whilst the enzyme takes care of the drainage aspect.

Dry end chemistry

The chemistry of the papermaking process can be divided into that taking place at the wet end of the paper machine (wet end chemistry) and that taking place at the dry end of the paper machine. The term "dry end chemistry" is not that widely used and the dividing line between them is not defined in any absolute terms, but a logical position is at the entry to the drying section where the sheet starts to experience elevated temperatures. In line with this definition, there are two distinct sorts of dry end chemistry:

- ❑ changes to the chemistry of materials already present in the paper web

  These are driven entirely by the increasing sheet temperature and are particularly important for all papers that are sized (see examples under AKD, ASA and rosin) or wet strengthened (see example under PAE resins) at the wet end. Curing is a useful term to cover the range of processes that take place in the drying section when sizing and wet strength chemicals are present. A useful side-benefit of having to dry paper is the inactivation of most micro-organisms in the paper through thermal denaturation of microbial proteins, so that the product at the reel, although not sterile, is of much improved microbial quality (see paper microbiology). For some grades of paper (eg newsprint), this may be the only substantive chemical change that takes place during drying.

- ❑ the surface application of chemicals at the size press, calender water box and coater.

  This is a very important set of processes for many grades of paper, but, equally, there are many grades (eg newsprint, tissue/towel and some packaging papers) with no surface application. Drying the surface-applied paper is still required and this can be important for the effective sizing (curing) of surface-sized papers. The types of chemistry that occur during surface application are similar to those described under wet end chemistry and colloid chemistry is again the most important of these. Reaction chemistry plays a minor positive role, as it does within wet end chemistry, but the likelihood of problematic interactions is not as high as at the wet end.

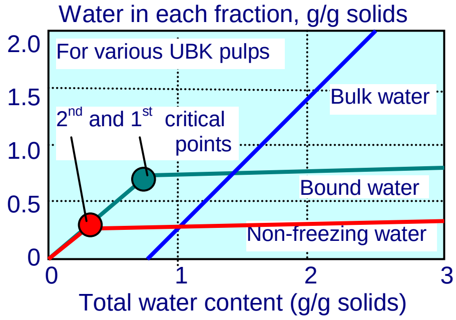
Drying

This is the final phase of water removal, but, on some paper machines, there may be three separate stages of drying - before a size press, between a size press and a coater and then final drying. At the inlet to the drying section, the paper web has a solids content of 40-55% depending on grade and on the efficiency of the preceding press section. Removal of the water remaining after pressing is influenced more than preceding stages by the chemistry of the paper web (eg its water-holding capacity), but a more open physical structure should still allow easier passage of water vapour. The high temperatures in the drying section are very important to the efficacy of some wet end chemicals (see dry end chemistry) and to the microbial quality of the paper at the final reel.

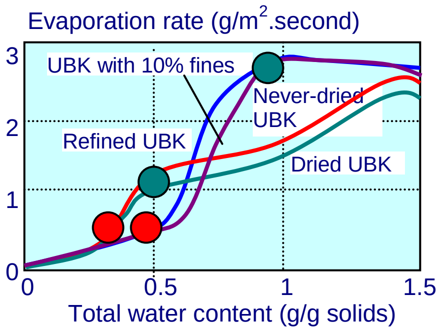
The overall drying process can be divided into 4 phases depending on the drying rate:

- ❑ warming period when the sheet begins to lose the bulk (unbound) water
- ❑ a period with a constant evaporation rate of the rest of the unbound water
- ❑ the first period when the evaporation rate declines after the so-called first critical point
- ❑ the second declining evaporation rate period after the second critical point.

The breakdown of pulp moisture into the various categories (unbound, bound, etc) is described under water removal. Some results of water removal across these different phases are shown in the three figures below for various forms of an unbleached Kraft (UBK) pulp. The first set of data (at right) shows the complete loss of bulk water before any significant loss of bound water, which only takes place above a solids content of 50%, ie during drying not pressing. Similarly, removal of the non-freezing fraction of the bound water starts only after removal of most of the freezing fraction.



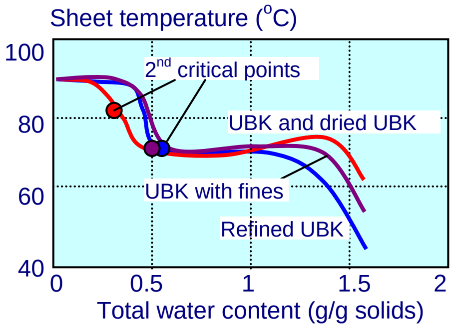
Source: Maloney et al, Paper Technology, 1998, 39, 6, 39-47.



Source: Maloney et al Paper Technology, 1998, 39, 6, 39-47.

Looking at drying in terms of the evaporation rate (figure at left), data for these 4 pulps falls into two categories depending on the level of fines (present through refining the pulp or back-adding pre-separated fines) rather than on their previous drying history. The first critical point (at about 55% solids content for the high fines-content pulps and 67% solids content for the low fines-content pulps) is below the pulps' fibre saturation point (see this table for WRV/FSP data for the same pulps). The first critical point is believed to be where moisture removal from macropores in the fibre wall is complete.

At the second critical point (at about 75% solids content for the high fines-content pulps and 70% solids content for the low fines-content pulps), the micropores have also collapsed and the residual water is the hydrogen-bonded water of hydration, which is the most difficult to remove. In terms of sheet temperature (see diagram at right), the second critical point occurs at a lower level in the high fines-content pulps, which may be due to a greater temperature gradient in the paper's z-direction. At this point, the fibres shrink appreciably, hydrogen bonds develop between cellulosic hydroxyl groups and the paper begins to develop its ultimate strength.



Source: Maloney et al Paper Technology, 1998, 39, 6, 39-47.

Dry strength agent

The dry strength of paper products is their most important property for virtually all grades. The precise reason for using dry strength agents depends on their point of addition:

❑ wet end addition to the stock suspension prior to sheet formation

Refining of pulps is the main way to increase the body strength of paper, but it has some drawbacks such as increased fines content (leading to impaired drainage and retention) and some changes in sheet characteristics may be undesirable, eg reduced bulk and porosity. The addition of dry strength chemicals provides a complimentary route to improving paper strength with none of these adverse side-effects. Generally however, chemicals tend to be used together with refining to give an overall optimum system in terms of machine productivity and product performance. Wet end dry strength additives are more uniformly distributed within the paper matrix, particularly in the paper's z-direction, than when added to the paper surface and thus improve the overall bonding within the sheet. Wet end dry strength additives are used in three main sectors:

- in filler-containing papers in order to compensate for the adverse impact of fillers on sheet strength
- in papers using recycled pulps in order to compensate for the inherently weaker fibres present
- in the making of some tissue grades in order to compensate for the absence of refining, which tends not be used in this sector as it decreases bulk and softness, both being important product characteristics for this grade.

- application to the paper surface by spraying or impregnation at the size press

  Here, the chemical tends to be concentrated at the paper surface to give a strong film and thus improve the surface strength of the paper. However, some penetration into the body of the paper may be desirable in some grades and this is controlled by the level of sizing in the base sheet and the viscosity of the added chemical solution. Surface addition of dry strength agents is used mainly in the following sectors:
  - in printing/writing papers to enhance surface properties
  - in packaging grades for improved overall stiffness
  - in boards for improved ply-bonding.

Coating formulations contain chemicals that might be used as dry strength additives, but their main function in a coating formulation is as a binder for the main pigment component.

Several different types of chemical are used for dry strengthening, but there are two main categories:

- natural water-soluble polymers
  - starches, which are used at the wet end and the surface and are the biggest category by far
  - gums, which have a relatively small market share for both wet end and surface application
  - carboxymethylcellulose, which are used mainly at the wet end (and in coating)

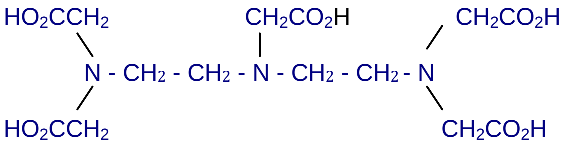
- synthetic water-soluble polymers
  - polyacrylamides, which are used only at the wet end
  - polyvinyl alcohol, which is used only for surface application.

DS

This is an abbreviation for degree of substitution.

DTPA

This is an abbreviation for diethylenetriamine-penta-acetic acid, which may be used as a chelant, although this is not common in papermaking. It is more widely used with bleaching chemicals such as hydrogen peroxide to prevent interference from metal ions.



Dyes

Dyes are the main type of colorant used in papermaking, accounting for at least 90% of the total market. They can be added at the either the wet end or the paper surface, but wet end addition is the more prevalent (about 95% of total). The ability of dye molecules to absorb light in the visible region of the electromagnetic spectrum is usually due to the presence of a system of conjugated double bonds within the dye molecule. The absorbed energy is normally dissipated by vibration of inter-atomic bonds. Being amongst the more expensive of papermaking additives, it is imperative that dyes have certain key characteristics in order to be used cost-effectively:

- good substantivity (adsorption) on the particulate matrix, notably for wet end addition
- good affinity (irreversible binding) to the substrate
- good fastness (stability) against exposure to conditions such as liquids, heat and light.

Dyes can be classified into two broad groups in accordance with their generic chemical character:

- traditional dyes developed from chemicals used for textile dying
  - acidic (anionic) dyes, which are little used now in papermaking (<5% of total) due to poor substantivity (and hence retention) and poor fastness characteristics.
  - basic (cationic) dyes, which are still used quite extensively (about 30% of total) due to acceptable performance combined with reasonable economy of use, but only for certain furnishes.
- direct dyes, which were developed to have better substantivity for and affinity to the fibre surface and, despite their higher unit cost than basic dyes, are now the main type of dye used in papermaking (about 60% of total). They are available either in an anionic or cationic form.

Certain groups can be incorporated in the dye molecule to shift the absorption to longer or shorter wavelengths (chromophores) or to deepen the colour (auxochromes). All dyes have a classification type and number in accordance with the international Colour Index (CI), but they can also be classified by their more detailed chemical character:

- azo dyes, which account for about 70% of all dyes in commercial use, notably in the traditional acid and direct dye categories.
- anthraquinone dyes, which, being small molecules, are little used in papermaking due to poor substantivity
- di/tri-aryl methane dyes, which are representative of many basic dyes and are also used as colour formers in carbonless-copy papers
- phthalocyanines dyes, which are used more widely as pigments than as dyes.

Today, there is little use of powdered dyes added to the pulper and most mills are using continuous dosing of liquid dyes for both wet end and surface application. As liquid products, the dye's solubility characteristics are important as high solution strengths are desirable in order to minimise volumes for transportation and storage. The incorporation of charged hydrophilic groups enhances the water solubility of dyes, which is one of the reasons why dyes are always charged molecules.

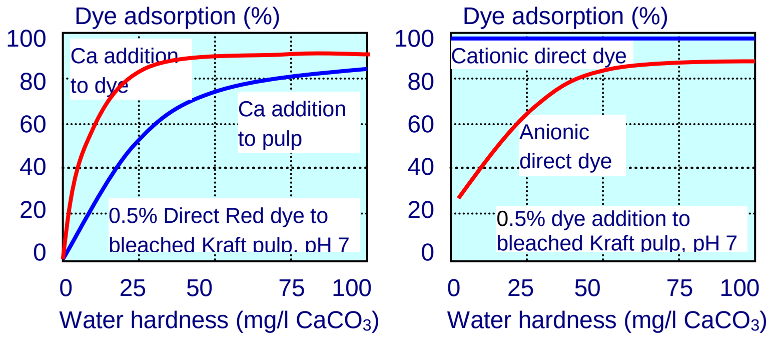
Many anionic dyes have this charge character through the presence of sulphonate groups, as this confers good solubility. The counter ion also influences solubility and anionic dyes are often in the form of their ammonium salt due to their greater solubility compared to sodium or potassium salts. Cationic dyes are inherently less water-soluble and often require high acid levels or organic counter-ions such as acetate for stability. Concentrated liquid dyes (up to about 40% strength) can be produced using auxiliaries such as so-called hydrotropic agents like urea and water-miscible organic solvents (eg alcohols and glycols), but this leads to contamination of machine water which may cause process or wastewater problems. In recent years, dyes containing no solubilising additives have been produced by subjecting the dye solution to ultrafiltration or reverse osmosis in order to remove the electrolytes which otherwise limit dye solubility.

As for all papermaking materials added at the wet end, the total retention of dyes depends primarily on their single pass retention, which is determined firstly by adsorption of the dye on the particulate matrix and then by the various processes that determine the single pass retention of the particulate matrix. The factor that differentiates the retention characteristics of dyes from that of other chemicals is that any retention-related lack of uniformity in dye distribution (mottle or colour 2-sidedness) is immediately evident, whilst that of other chemicals (eg strength additives) is only apparent once the paper is tested or used.

The critical stage in single pass dye retention is the initial adsorption and there are several possible mechanisms for this:

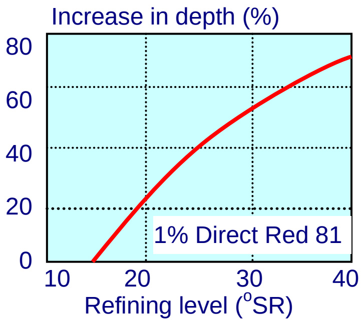
- electrostatic forces between charged groups on the particulate surface and charged groups on the dye molecule, which can take two forms:
  - electrostatic attraction between the anionic particle and a cationic dye
  - electrostatic attraction between the anionic particle and anionic dyes through the agency of cationic agents that are naturally present (eg calcium ions), added for that or other purposes (eg aluminium salts such as alum or PAC) or specifically added as dye fixatives (normally cationic polymers such as those based on dicyandiamide)
- hydrogen bonding between hydroxyl groups on cellulose and hydroxyl or various nitrogen-containing groups on the dye molecule
- van der Waals attractive forces, particularly between the fibre surface and the linear, planar molecules that constitute direct dyes.

The charge-related adsorption of dyes is influenced by the normal range of wet end factors that affect the performance of all charged water-soluble additives. The most important are the presence of other dissolved substances (usually of opposite charge to that of the dye), that can precipitate the dye and the concentration of dissolved cations. The latter has been a particularly important issue for mills using anionic dyes as they have moved away from acid papermaking with alum to neutral papermaking. The results shown here (left-hand picture) corroborate the well-known effect of calcium hardness in aiding anionic dye retention. They also indicate that the active adsorbing entity (in the presence of calcium ions) is a Ca-dye complex rather than the anionic dye adsorbing on fibre with its anionic sites in the calcium form. The second picture (far right) shows the inherent advantage of cationic direct dyes in that their performance is high irrespective of the calcium level.



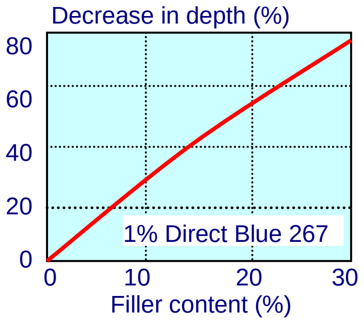
Source: Guender and Pfohl in Proceedings 1987 Pira Neutral Papermaking Conference.

The nature of the furnish determines the surface area of the particulate material that has to be covered and the surface charges available for electrostatic attraction. The refining of pulps increases the fines content and hence the surface area available. In the example at right, this improves overall dye retention and the level of coloration effect, although this does depend on efficient fines retention.



Source: Colling in "Applications in Wet End Chemistry", Blackie, 1995. Chapter 8. 120-138.

The presence of mineral fillers in printing/writing paper grades is important as dyes have little affinity for mineral surfaces and their high surface area increases dye consumption to achieve a particular shade (as shown at right below in terms of the loss of colour at constant dye dose with increased filler). When fillers are present, the single pass retention of the whole fines fraction (including adsorbed dyes) is particularly important in order to minimise colour 2-sidedness and coloration of the whitewater. Once retained in the fibrous web, dyes with a poor affinity for the particulate surface may migrate with the water flow thus exacerbating 2-sidedness. This is most prevalent in the drying section where the high temperature conditions facilitate migration of dyes with poor heat fastness.



Dosing of liquid dyes at the wet end is often controlled by on-line colour measurement at the dry end. Although each coloured grade could be made by the addition of a dye pre-mixed by the manufacturer, this would necessitate the storage of many different dye formulations so the normal system is for the computer-controlled dosing of several dyes to give different colours. Rapid dispersion of the dye throughout the stock is essential in order to avoid localised coloration and possible mottle in the product. The best location of the dye dosing point and the order of addition of dye and other chemicals depends on each system’s chemical balance. Dyes are expensive materials and, whilst only small amounts (up to 0.1 kg/tonne paper) are needed for lightly-coloured (tinted) grades, much larger quantities are necessary for deep shades (up to 50 kg/tonne paper) in which cases dye costs can equal and sometimes exceed fibre costs.

Dye addition to the paper surface can be made by all the normal surface application techniques - the size press, water boxes on machines with calenders and, for coated papers, at the actual coating stage. The main competitor to wet end dye addition is addition at the size press, which normally means initial dye addition to a starch solution. The key criterion for dye selection is chemical compatibility with the size press starch and any other additives used. As the size press starch is usually nonionic to weakly anionic, the most commonly-used dyes for this application are anionic direct dyes, which bind well with starch. The potential advantages of size press dye addition are the normal benefits associated with size press addition of any chemical - good efficiency of use due to effectively 100% retention and the added chemicals being concentrated towards the surface of the paper. For dying, there is a strong grammage-related efficiency effect because less dye is required to achieve a certain colour level as the grammage rises above 100 g/m^2 and is about 50% of the wet end dose at 300 g/m^2.

Notwithstanding this advantage, improvements in the efficiency of wet end dying over the last 20 years (due to use of more effective dyes) have eroded some of the potential advantages of size press dye addition and there are also some difficulties for dying at the size press:

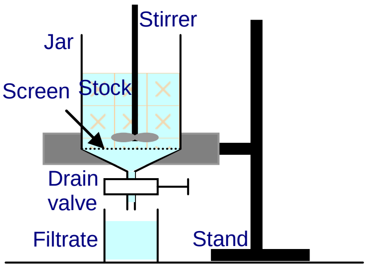
- poor uniformity of coloration across the surface on one side (mottle or orange peel effect), which can be caused by many factors related to the uniformity of the starch pick-up and penetration. The severity of this problem can be reduced by split dying, part at the wet end and the rest at the size press. This also minimises some of the difficulties caused by the recycle of coloured broke (colour variation in the base paper) when dying is done only at the size press.
- poor uniformity of coloration between the two sides, usually caused by different absorption characteristics which may in turn be caused by wet end sizing-related issues
- impaired bleed-fastness due to the dye's concentration at the surface and its association with water-soluble starch. This problem can be reduced by the use of starch insolubilisers.
- drift in coloration due to the relatively-long equilibration time when making dose corrections and changing colours.

Similar considerations apply to the use of dyes in coating such that anionic dyes (mainly directs) are again the most common type. If a coloured coated paper is required (not that common), the only option is coloration at the coating stage as the colour of the base paper is largely, but certainly not completely, masked by the coating layer (depending on its thickness). A special type of dye added at the coating stage is the micro-encapsulated dye precursors used in carbonless-copy and thermal papers.

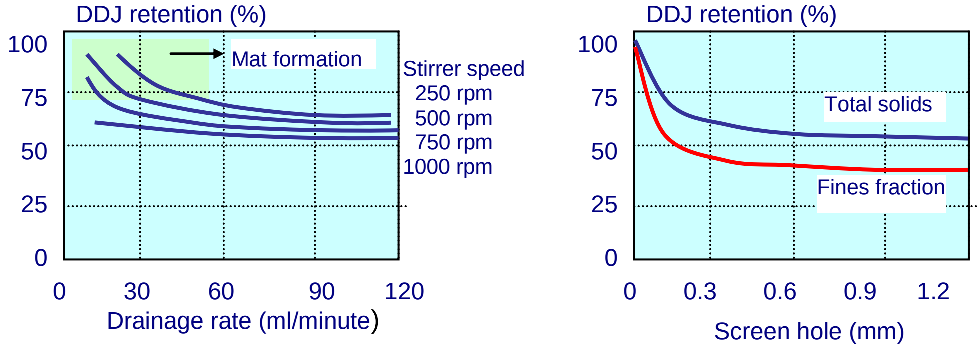
Dynamic drainage jar (DDJ)

This is the most commonly used system for laboratory measurement of retention and was developed by Ken Britt of the Empire State Paper Research Institute (ESPRI) in the early 1970s. The concept of the DDJ has been adapted by many companies to produce their own versions, which sometimes also allow sheets to be produced. The most recent version is the Dynamic Filtration System from BTG-Mutek.

The DDJ (see right) is extremely simple in design consisting of a barrel that screws into a round base containing a screen, support plate and drain hole as shown above. The barrel contains 3 vanes along its length to prevent vortex formation on stirring. A standard 3-blade impeller is located a set distance (3.2 mm) above the screen and its speed is controlled in the range 100-3000 rpm. The purpose of stirring is two-fold - to prevent mat formation and to subject the stock to controlled shear. The shear rates in the DDJ are 1000 second $^{-1}$ at a stirrer speed of 250 rpm increasing to 6000 second^{-1} at a stirrer speed of 1000 rpm.



The jar outlet is fitted with a rubber stopper containing a 6.4 mm glass tube leading to a rubber tube fitted with a clamp and finally a tapered glass tube. It is important to control the rate of drainage in order to preclude the formation of a mat on the screen during drainage (see left below), which occurs when the drainage rate is too slow. An optimum is around 60 ml/minute. The standard screen used with the DDJ is the 125P screen, which has 76 micron openings corresponding to 200 mesh. Not surprisingly, increasing the size of the screen holes lowers the measured DDJ retention value as shown at right below. It is common to use a sample of the wire from the paper machine of interest where this is appropriate.



Source: Pelton in Proceedings Tappi Retention/Drainage Seminar, 1979.

As the concept of the DDJ is to drain the stock whilst stirring at the selected speed, the retention values produced reflect only the hetero-/homo-aggregation of fines with fibres and not the straining of fines through a fibrous mat. The standard retention technique involves placing 500 ml of stock of known consistency in the jar and commencing stirring at the selected speed. A dose of retention aid(s) is added and stirred for the requisite time before opening the drain valve. The filtrate is collected for 30 seconds, by which time about 120 ml should have been allowed to drain.

The filtrate is filtered through a standard filter paper and the retention calculated as below:

$$\text{DDJ retention (\%)} = 100(C_1 - C_2)/C_1$$

where C_1 = stock consistency and C_2 = filtrate consistency.

The DDJ retention can also be calculated in terms of the fines component of the furnish, but this requires an initial measurement of the furnish's fines content, which is the second application of the DDJ. In this technique, the sample of known consistency is placed in the jar and the fines are washed through the standard screen by passing at least 2 litres of water (with added dispersant) through the jar until the filtrate is clear. The weight of solids remaining in the jar is measured and the fines content (% material below 200 mesh) calculated by difference.

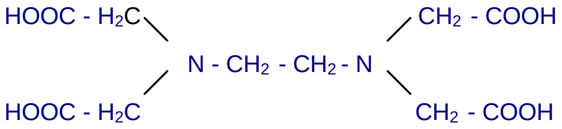
Some typical data for DDJ retention versus stirrer speed for various chemical regimes are shown here. It is possible to try to match the retention on the DDJ with the wire retention on individual machines by using machine wire in place of a standard screen and by adjustment of the DDJ stirrer speed. This produces a so-called "Hydrodynamic Index" for each machine, but it should be noted that, due to the absence of mat formation in the DDJ, the DDJ retention will always be worse than the machine retention at similar levels of shear. As the stirrer speed is raised, the DDJ retention approaches the value for the non-fines content of the stock, assuming that wire in use has holes no larger than those of the standard 125P screen used to determine the fines content.

ECF

This abbreviation stands for elemental chlorine free in relation to bleached chemical pulps and pulping processes.

EDTA

This is an abbreviation for ethylenediamine-tetra-acetic acid, which may be used as a chelant, although this is not common in papermaking. Its formula is shown at right.

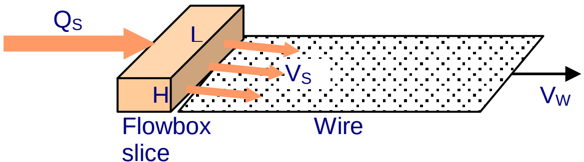


$(HOOC-H_2C)_2N-CH_2-CH_2-N(CH_2-COOH)_2$

Efflux ratio

This is a measure of the forward velocity of the papermaking stock (V_S) as it is projected from the flowbox slice compared to the velocity of the papermaking wire (V_W) onto which the stock is projected (see diagram at right). It is also known as the jet-wire speed difference or ratio. There are three possible operating conditions:

- $V_S = V_W$, ie zero efflux ratio
- $V_S > V_W$, , ie efflux ratio > 1 known as "rush" forming
- $V_S < V_W$, efflux ratio < 1 known as "drag" forming.



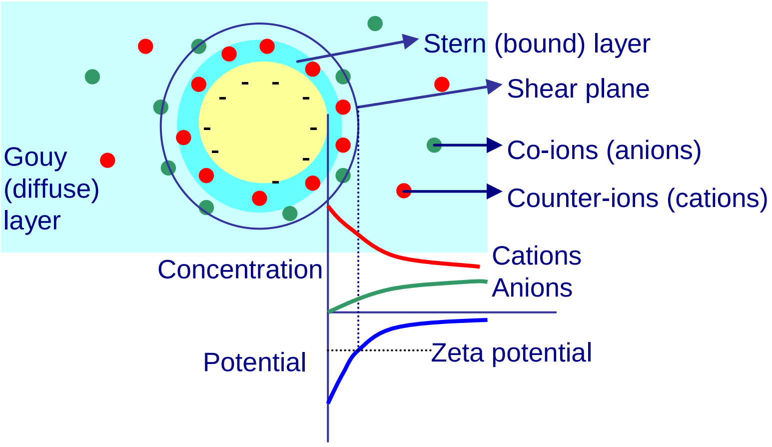
$V_s = Q_s/HL$

The efflux ratio is particularly important in relation to the formation quality of the paper and is often set to optimise this aspect of paper quality. Efflux ratios slightly less or slightly greater than unity (0.97-1.03) tend to give improved formation and less fibre alignment in the machine direction (ie squarer sheet), but can also change fibre orientation in the z-direction. Rush forming tends to give fibres some z-directionality with a forward tilt (ie leading end pointing downwards) and drag forming tends to give fibres some z-directionality with a backward tilt. These effects do also depend on the design of the former and the angle of impingement of the stock jet on the forming fabric.

Electrical double layer

This term refers to the distribution of ions surrounding charged particles. The particle surface acquires a charge for various possible reasons and this influences the distribution of ions in the liquid adjacent to the surface. Various researchers (eg Chapman, Helmholtz, Gouy, Stern) have been associated with the theoretical treatment of this phenomenon and have lent their names to the various layers within what has become known as the electrical double layer (see figure below for a negatively-charged particle).

The distribution of ions results from the net effect of attraction to the particle surface through electrostatic or van der Waals forces against the thermal forces of motion. Ions of opposite charge to the surface charge are attracted to the surface, some becoming bound in the Stern layer and others being held more diffusely in the Gouy layer. Ions of like charge to the surface are repelled and their concentration increases with distance from the surface (in contrast to that of the counter ions), but the overall net charge within the double layer is zero. Outside the double layer in the bulk solution, there is a uniform average charge distribution.



The precise relationship between potential and distance from the particle surface is complex and depends, amongst other things, on the shape of the surface (ie flat or spherical). In the simplest form of this relationship (as indicated in the picture above), the potential decreases exponentially with distance from the charged surface:

$\Psi = \Psi_S e^{-\kappa x}$ where Ψ_S is the surface potential and x is the distance from the surface

The term "κ" is the Debye parameter and has the units of reciprocal length. Its reciprocal (1/κ) is a measure of the size of the double layer and is usually referred to as its thickness or the Debye length.

An important characteristic of the electrical double layer is the zeta potential (ξ) which is the potential at the plane of shear. This is located slightly on the outer side of the interface between the Gouy and Stern layers. The particle and associated ions within this envelope move together when subjected to shear or an applied potential. The zeta potential is thus somewhat smaller in absolute value (whether negative or positive) than the surface potential.

The potential of the particle surface (in volts or, more commonly, millivolts) depends on its charge density (σ in units of coulombs/m^2). This relationship can be approximated by the following equation at low potentials:

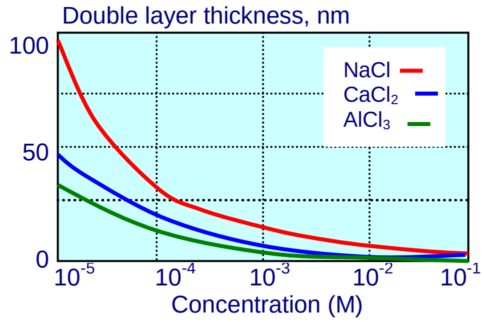
$\Psi_S = \sigma/\varepsilon\kappa$ where ε is the permittivity of water

At a constant surface charge density, the surface potential thus varies with the double layer thickness. For a charge-stabilised particle, a reduction in double layer thickness (increased κ) means that the surface potential declines as the surface charge density must remain constant (provided that the reason for the decline in thickness does not change the ionisation of surface groups or the adsorption of ions that are responsible for the charge). The thickness of the double layer is thus a very important parameter in relation to particle aggregation. It can be calculated from the following equation:

At $25^{o}C$, $1/\kappa$ (nm) = $1/(3.28cz^2)$ where c = molar concentration of counter ions with valency z

This thickness parameter is plotted against distance in the figure below for various electrolytes. This shows that the double layer thickness decreases quite rapidly with increased concentration, particularly for multivalent counter ions, such as calcium or aluminium in the case of a negatively-charged surface. Simple electrolytes are never used to promote particle aggregation in papermaking although alum has, of course, been used for various functions whereby this effect would come into play. Nevertheless, electrolytes that are present in a suspension (albeit rarely at high levels by deliberate addition) do influence the electrostatic repulsion between charged particles and thus their state of aggregation. As wet end electrolyte concentrations exceed (and, in many cases, greatly exceed) 0.001M on most paper machines, the double layer thickness is likely in practice to be no more than about 10 nm.

This effect of electrolytes on particle aggregation is manifest in the Schulze-Hardy Rule, which ranks the effectiveness of ions of different charges in destabilising colloidal dispersions. It should be noted that increased electrolyte levels influence many other wet end phenomena (eg the efficacy of retention aids), which may outweigh what may seem, at first glance, to be a benefit in relation to promoting particle aggregation.



Electrochemical treatment

This is a recently-developed technique to stop slime formation within papermaking systems. This involves the application of an electrical potential through the placement of an electrode or array of electrodes within a metal pipe or tank. Obviously, this would not work in non-metallic systems. This approach has been investigated independently at about the same time by two companies - Zeta Corporation in North America and Savcor Process Oy in Finland - although the two concepts are quite different.

The process from Zeta Corporation calls itself an electrostatic approach in which a capacitor is set up from an inserted electrode/ceramic dielectric (the Zeta Rod^{TM}) and the grounded body of the pipe or tank. One mechanism at work here is for the high applied voltage (30-35 kV DC) to increase the surface charge on particles and thus make them less likely to aggregate together. As this would not be a good idea within the stock approach system, the examples quoted are on showers using recycled water where blockages from fines and slime are an ever-present headache. A Canadian mill has used this system on two paper machines to stop slime growth within a press shower system using in-line filtration. Continued running with a 50% reduction in biocide addition has yielded an 80-85% drop in plugging of shower orifices combined with a pay-back time of 2 months.

The Finnish approach is different, not least in that the applied voltage is much lower and that it works by changing the surface conditions at the metal surface. Depending on the chemistry of the water surrounding the metal surface (M), a number of reactions may take place at both the anode, where oxidising reactions always take place and the cathode, where reducing reactions always take place:

Anode reactions: $M \rightarrow M^{n+} + ne^-$
$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

Cathode reactions: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

It is evident that several of these reactions affect the pH in the vicinity of the metal surface and this cycling of surface pH in response to managed changes in the applied voltage is what is believed to limit microbial attachment. As the application of an inappropriate voltage could exacerbate corrosion, it is critical to optimise the electrochemical conditions for each application. After small-scale testing in a simulator, an electrochemical treatment system has been installed at a Finnish mill producing coated fine paper and operating at neutral pH. Six electrodes were placed in the stainless steel cloudy filtrate tank after the machine saveall and this kept the tank clean for about one year. There is at least one other installation at a Swedish mill.

Electrochemistry

This subject is part of physical chemistry and is concerned with the interconversion of electrical and chemical energy. This is not a mainstream topic within papermaking chemistry, but it is important in relation to the corrosion that takes place to varying degrees in most papermaking systems and also to a recent method developed for slime control.

There are in two basic types of electrochemical cell:

- Galvanic cells

  These cells convert chemical energy into electrical energy in a spontaneous way when the two electrodes are connected. The best example of this is the connection of two dissimilar metals, when a current will flow from the anode (where one metal is oxidised) to the cathode (where a reduction takes place). Galvanic cells within the same metal structure are also responsible for corrosion reactions.

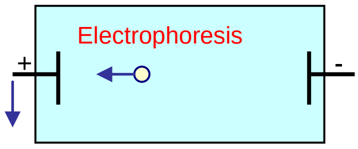
- Electrolytic cells

  These cells convert electrical energy into chemical energy through applying an external current. These processes are used to manufacture chemicals, a good example being the electrolysis of sodium chloride to produce chlorine and sodium hydroxide. The application of an electric current in this way is also used to protect metal structures from corrosion.

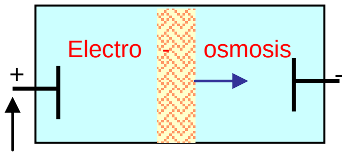
The terminology of anode/cathode for each electrode can be confusing as they are assigned different charges in galvanic and electrolytic cells, but, in both cases, oxidation always takes place at the anode and reduction at the cathode. Each reducing-oxidising couple develops an electrical potential depending on the ease of electron removal/acceptance and these are termed redox potentials, which can be useful to measure in papermaking systems as an indication of the presence or absence of dissolved oxygen. The equilibrium potential of a cell is the potential when there is no current flowing - the cell is said to be polarised when its potential is changed from the equilibrium value by the application of a current. This relationship between potential and current is termed the polarisation curve and the difference between the equilibrium and actual potentials is the cell's over-potential.

Electrokinetics

This is the general term given to the four kinetic effects resulting from the presence of the electrical double layer around charged particles. They can all be used to measure the particle's zeta potential and are illustrated in the figures below where a downward arrow signifies a generated potential and an upward arrow signifies an applied potential:

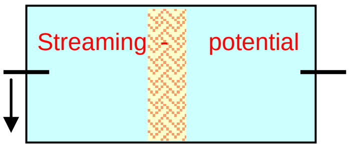


- electrophoresis, which is the movement of the free, charged particle under an applied potential. This is widely used in papermaking as an off-line laboratory technique.

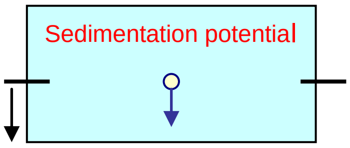


- electro-osmosis, which the movement of the liquid phase under an applied potential when the charged particles are restrained from movement. It has not so far been harnessed for practical charge measurement.

- streaming potential, which is the potential generated when the liquid phase is passed through immobilised charged particles. A variation of this technique (streaming current) is used to measure dissolved charges. Both techniques are widely used in papermaking on both off-line and on-line modes.



- sedimentation potential, which is the potential generated when the charged particle falls through the liquid phase. It has not so far been harnessed for charge measurement on papermaking samples.



Electrolytes

The formal definition of an electrolyte is a substance that can dissolve to give a solution of ions capable of conducting an electric current and is usually quantified by measurement of conductivity. The level of electrolytes is important mainly in relation to wet end chemistry, as the levels of electrolytes at the size press (excepting where sodium chloride is deliberately added) and in aqueous coating are usually low. Being dissolved inorganic solids, electrolytes are one of the two important sub-set of the total dissolved solids present at the wet end, the other being dissolved organics.

There are three possible sources of dissolved electrolytes at the wet end:

- those taken in with the fresh water to establish the baseline concentration.

  This is usually quite significant as most natural waters contain measurable levels of ions such as calcium, sodium, etc and preliminary water treatment processes at mills do not normally affect the dissolved solids fraction.

- those derived from other raw materials which can be further sub-divided into:
  - electrolytes added directly to the wet end, eg alum and PAC, but this contribution should be low as these chemicals are primarily selected on the basis of their high adsorption on the particulate matrix. However, the sulphate component of alum is usually left behind in the liquid phase after alum has hydrolysed, so there can be significant levels from wet end additives.
  - electrolytes which are present in particulate materials (pulps, broke, calcium carbonate), but which then dissolve in the liquid phase. This source includes residual electrolytes from pulping/bleaching chemicals that are left in pulps, sodium chloride from the recycling of size press-treated broke containing added salt and the interaction between calcium carbonate filler any wet end acidity, which dissolves both ions.

At the wet end, the baseline level of electrolytes from fresh water would not normally exceed a conductivity of about 0.5 mS/cm and can be much lower than this level. The main electrolytes derived from fresh water are sodium, potassium, calcium and magnesium cations balanced by chloride, sulphate and bicarbonate anions. The electrolyte concentration at the wet end is never managed pro-actively, but is determined by the baseline level plus the effect of the degree of water closure on the input load from other sources (see this example for the general pattern of concentration build-up on closing up). Observed wet end levels range from conductivities below 1 mS/cm for machines with a low/modest fresh water concentration and low input load to as high as 10 mS/cm at recycled mills with substantially closed water systems and a high input load.

The level of electrolytes at the wet end is important for several reasons:

- their effect on the size of the electrical double layer surrounding charged particles and thus on the ease of particle aggregation in the absence of polymeric retention aids (see this example for the effect of electrolytes on pulp retention and charge and these examples of their effect on the charge of calcium carbonate particles).
- their effect on the conformation of polymers, which has a significant effect on their adsorption and mode of action (see examples of the effect on adsorption of polyacrylamide, cationic starch, amphoteric starch and PAE resin)
- their effect in shielding the electrostatic forces between particles (see example here for AKD size retention and here for pitch stability) and between particles and added polymers (see here for adsorption of cationic starch on a bleached Kraft pulp)
- their effect on the form of anionic groups attached to the fibre through the Donnan effect on ion exchange and their consequent effect on the swelling of pulps and thus on:
  - the conformability of fibres and hence the ultimate strength of papers (see this example)
  - the dissolution of substances (notably polymers) from pulps (see this example for bleached Kraft pulps and this example for unbleached Kraft pulp).

Given the nature of these effects, it is clear that the overall impact of electrolyte levels on critical wet end parameters such as particulate single pass retention is complex. Increased electrolyte levels promote natural inter-particle aggregation, but this would only be important on low-shear paper machines due to the poor strength of these aggregates. The impact of electrolyte levels on the efficacy of retention aids is thus more important on most paper machines. The compression of the electrical double layer at increased electrolyte levels and the consequent closer inter-particle approach may assist certain retention aid polymers that function by a bridging mechanism - the deliberate addition of electrolytes for this purpose is sometimes referred to as sensitisation. However, increased electrolyte levels also tend to reduce the extension of polymer chains, which itself has a complex effect on polymer adsorption due to accessibility factors. This is discussed further under polymers.

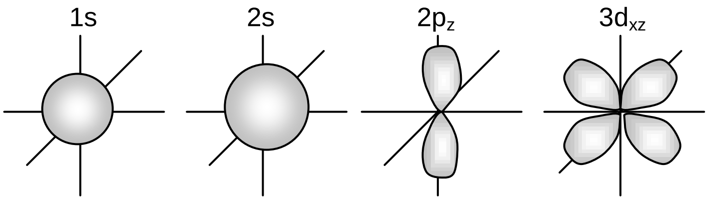
Depending on which of these effects pre-dominates, increased electrolyte levels could increase or decrease polymer adsorption. The examples cited above also show the importance of the character of the individual ions. In papermaking, the ion with the strongest impact on polymers (cationic and anionic) and which also shows considerable variability in its concentration is calcium. Generally, this ion will aid the adsorption of anionic polymers (and other anionic additives such as dyes) and impair the adsorption of cationic polymers and its level will thus profoundly influence polymer selection. The last of the three generic electrolyte effects listed above (the dissolution of organics from pulps) adds to the complexity through its impact on the level of anionic trash.

One thing is clear about electrolytes and this is that, given their pervasive influence on wet end chemistry and hence on the functionality of paper chemicals, it is essential that electrolyte levels at the wet end are closely monitored via their conductivity. In most cases, it will be beneficial to minimise the intake of electrolytes with raw materials and their generation (eg $CaCO_3$ dissolution) in the process. At the very least, this will minimise the variability in wet end electrolyte concentrations and allow the selected raw materials to function effectively and in a uniform manner over time. There is one reported circumstance where moderate electrolyte levels are claimed to be quite beneficial and this is on paper machines using calcium sulphate as a coating pigment. This is attributed to the fact that the wet end system is then effectively buffered at a constant electrolyte level corresponding to the solubility of calcium sulphate (about 2 g/l).

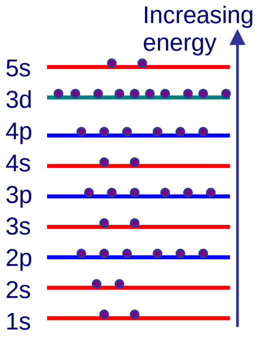
Electron

This is a tiny elementary particle with a mass of 9.11 x 10^{-28} g that is responsible for the negative charge on molecules and other materials. The charge of one electron is 1.6 x 10^{-19} Coulombs. The electron is present in all atoms, where their negative charge matches the positive charge from protons in the nucleus of each element. The arrangement of electrons around the nucleus is very important in determining the valency (or valencies) of each element and their chemical properties. The original concept of electrons following defined circular orbits around the nucleus was replaced many years ago by the concept of atomic orbitals, which are areas of space around the nucleus within which the position of the electron can be defined with a certain probability.

Each electron is defined by a set of four quantum numbers, which refer to the size of its orbital (labelled "n"), the shape of the orbital ("l"), the momentum of the electron ("m") and the electron's direction of spin ("s"). For each combination of the "n" and "l" quantum numbers, the probability of the electron being in a certain position at a certain time or having a certain energy can be calculated from Wave Equations. It is not possible to know both the position and energy of an electron with a high probability due to the Uncertainty Principle. When atoms join together to form covalently-bonded molecules, the atomic orbitals are combined to give molecular orbitals.



As the elements increase in atomic number, elements are added to orbitals of increasing energy level. Orbitals are labelled with the letters s, p, d and f, each of which has a characteristic shape (see representation at right) and a maximum number of electrons (s=2, p=6, d=10, f=14). The first (lowest energy) orbital is designated 1s and (like all s orbitals) is spherical in shape and centred around the nucleus. The electronic configuration of hydrogen is 1s (one electron in the 1s orbital) and the electron is most likely to be found somewhere in the region of the centre of the spherical 1s orbital. The electronic configuration of helium is $1s^2$, the subscript denoting that helium has 2 electrons in the 1s orbital, each spinning in opposite directions. This represents a full s orbital, which is a particularly stable configuration and explains helium's chemical inertness.



Subsequent electrons in later elements are added to orbitals in the order shown at right with the f orbitals starting after 5d with 4f. The p orbitals have a dumb-bell shape (see picture above), with one along each axis, so can take a maximum of 6 electrons. The shape of d (see picture above for one of them) and f orbitals is more complex, but all have the greatest stability when they are full. The inert gases (Group 18 of the Periodic Table) are so called as each of their orbitals is complete and hence stable. However, as their atomic number increases (and the attraction force between the nucleus and the outermost electrons declines), even they (notably Xenon) can lose electrons and form covalent bonds with other elements (eg XeF_4). A complicating factor is that orbitals can be mixed or hybridised to create lower energy orbitals with new shapes and this can influence the element's valency.

Electrophilic

This term applies to elements or groups that have a strong tendency to attract or accept electrons. Electrophilic elements (such as chlorine) tend to be located at the right-hand side of the Periodic Table. The electrophilic character of some chemical groups (such as keto and azo) gives rise to an uneven distribution of electrons within some organic chemicals, which is particularly important for some of their reactions and for the functional properties of certain organic substances, eg dyes and fluorescent brighteners. The opposite type of element or group is termed nucleophilic.

Electrophoresis

This is one of the four possible electrokinetic techniques for measuring the zeta potential of particles. Electrophoresis takes place when a charged particle moves under an applied electrical potential. The velocity of individual particles or the particle cloud is measured by observation through a microscope or video camera or by laser techniques. Due to the small size of the measurement cell, the sample must contain only small particles (the fines fraction of a pulp or even a filtered sample). The measured output is the particle's electrophoretic mobility, which is the particle speed per unit potential gradient and has the general units of length^2 time^{-1} volt^{-1}, but is most commonly expressed as µm/second per volt/cm or µm.cm/volt.second (see these examples for pulp, for filler and for pitch particles).

There are several conceptual difficulties in converting electrophoretic mobilities to zeta potentials, not least the irregular shape of fibrous particles and some fillers. The most-commonly used equation is that due to Helmholtz-Smoluchowski, which assumes that the electrical double layer is very small compared to the particle size and that the surface conductance is small:

$$\text{Zeta potential (ZP)} = \text{EM}.\ \eta/D$$

where EM = electrophoretic mobility
η = viscosity of the liquid
D = dielectric constant of the liquid

There are many commercial laboratory instruments using this principle (from Brookhaven Instruments, Chemtrac, Lasertrim, Malvern Instruments, Rank Brothers, etc), but it is definitely not possible to use this technique on-line.

Electrostatic forces

These forces exist between all materials that have a charge. They are important in papermaking in relation to the interactions between many substances (both particulate and dissolved) within the papermaking wet end (see this diagram) and in coating mixtures. Particles at the wet end and in coating mixtures usually have the same charge character (most commonly negative) and inter-particle repulsion is thus the norm. At the wet end, the objective is to minimise the repulsive force in order to promote controlled particle aggregation (notably of the fines fraction), but, in coating, the objective is to maximise the repulsive force in order to arrest any tendency for particle aggregation and thus maintain a uniform coating dispersion.

The repulsive force between particles of like charge can be calculated from several equations of slightly different form, one of the more simple being as follows:

$$\text{Electrostatic repulsive force, } V_R = \frac{k.f^{\,2}.d.\exp(-H/K)}{z^2}$$

where f = term involving the surface potential, d = particle radius,
H = inter-particle distance, z = valency of counter ions
and K = measure of thickness of the electrical double layer.

It is thus evident that, unlike the van der Waals attractive force which is not affected by surface charge, the electrostatic repulsive force is influenced by external factors such as:

- ionic strength, which affects the thickness of the electrical double layer and
- pH, which affects the surface charge (f term) through its effect on ionisation of functional groups.

For charged dissolved substances (notably organic polymers) at the wet end, there are two very important sorts of charge-mediated interaction:

- the usually desirable attraction between dissolved cationic additives and negatively-charged particulates, leading to the additive's adsorption
- the undesirable attraction between negatively-charged dissolved solids (anionic trash) and cationic additives, leading to inactivation of the additive.

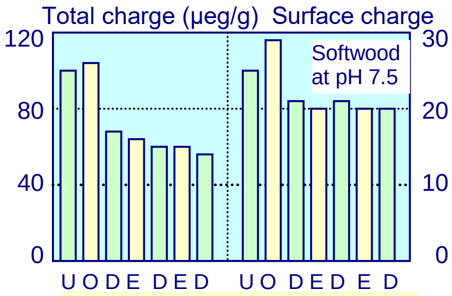
Electrostatic interactions between dissolved solids may also take place at the size press and coater, the main potential problem being between water-soluble materials extracted from the base paper and size press/coating additives. Undesirable interactions between different size press and coating additives should not be a problem as this is taken into account in the initial selection of such additives.

Elemental chlorine free (ECF) pulps

These pulps are produced without the use of chlorine gas or sodium hypochlorite and they have become the most common type of bleached chemical pulp (notably Kraft) over the last 10 years or so. This change has been driven by the environmental problems associated with chlorine bleaching, notably the generation of chlorinated organic by-products such as chlorinated phenols (eg pentachlorophenol), dioxins and chloroform. The ECF term should not be applied to bleached mechanical pulps as these have never been bleached with chlorine.

ECF pulps are produced from both hardwoods and softwoods using similar combinations of bleaching chemicals, a typical sequence being ODEDE$_{OP}$D, where O stands for oxygen, D for chlorine dioxide, P hydrogen peroxide and E for extraction with caustic soda. In view of their lower lignin content, shorter bleaching sequences (such as ODED or ODEDD) are sometimes used for hardwoods. In all ECF sequences, it is the oxygen and chlorine dioxide that have taken over from chlorine as the main delignifying agents, but the second extraction stage is often reinforced (as in the first sequence quoted above) with small quantities of oxygen and hydrogen peroxide to improve its efficiency.

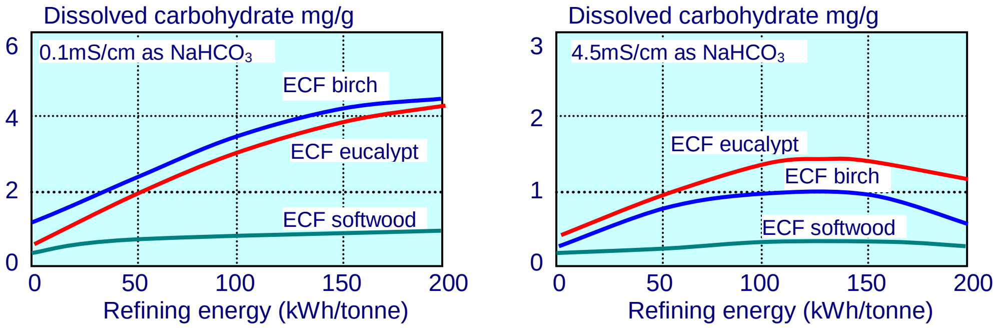
The profile of anionic substances through a typical ECF bleaching sequence for a softwood pulp is shown in the figure at right. A small increase in charge is evident after the oxygen (O) stage, probably due to introduction of new carboxyl groups, but the total charge then declines steadily through the remaining stages. The surface charge (that accessible to a high molecular mass polydadmac polymer) is less affected by bleaching than the total charge so that the proportion of charged substances on the surface of this particular pulp increases from about 25% in the unbleached pulp to about 40% in the final bleached pulp, ie ECF bleaching selectively removes more of the charged substances within the pulp's internal structure. This is a much higher proportion of the total charge than in other pulps shown in this table (about 20%). Hexenuronic acids accounted for about 25% of the total charge, but virtually none of the surface charge, indicating that they are located well within the fibre wall.



Source: Laine, J in Paperi ja Puu, 1997, 79, 8, 551-559.

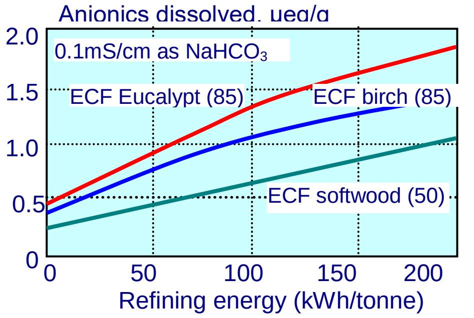
The resultant ECF pulps are not that different from the traditional chlorine-based bleached chemical pulps in terms of strength, brightness and chemical content (except for the lower level of residual chlorinated organic by-products, but these were never important in terms of the papermaking value of the original pulps). As with bleached Kraft pulps generally, these pulps are characterised by low levels of charged substances and of organics that could dissolve in the papermaking system. The levels of anionic substances in ECF pulps are typically as shown in the example above for softwoods (ie no more than about 50 μeq/g), but, as shown in this table, may be higher in some hardwood pulps (70-100 μeq/g depending on titration technique for eucalypts). Further data on anionic levels in hardwood and softwood ECF pulps is shown here.

As with all bleached Kraft pulps, hemi-celluloses are the main materials that may dissolve on initial slushing of the pulp. When pulps are refined after slushing, further dissolution takes place as the fibrous structure is opened up by mechanical action. This is illustrated in the figures below, which indicate that, at low electrolyte concentrations in the water, dissolution of carbohydrates is significantly greater from hardwoods than from softwoods. However, due to their adverse effect on fibre swelling, increased electrolyte levels substantially reduce dissolution for all pulps, but particularly for hardwoods. It is also evident that, at high refining and electrolyte levels, dissolution of carbohydrate starts to decline. The refining curve shown in these graphs is produced by refining the pulp at a fixed energy input for increasing time, so a decrease in dissolution means that material dissolved in the earlier part of the refining period is re-adsorbed, presumably onto fresh surfaces that are continually being created.



Source: Sjostrom in Nordic Pulp Paper Research J, 2000, 15, 5, 469-475.

Within the dissolved carbohydrate fraction there are anionic hemi-celluloses, which, when dissolved, become part of the anionic trash. This is illustrated at right for the same pulps as in the above figure, where the number in brackets after the pulp is its total charge content in μeq/g. Dissolution of charged organics follows the same pattern as for carbohydrate, but it is evident that only a small fraction (<2% in these cases) of the anionic substances dissolve during refining. This is desirable for all pulps, but particularly for bleached chemical pulps because of their relatively low content after bleaching. The anionic charge remaining on the pulp can then act as an adsorption point for cationic additives.



Source: Sjostrom in Nordic Pulp Paper Research J, 2000, 15, 5, 469-475.

Emulsion

An emulsion is a finely-dispersed mixture of two immiscible liquids, usually water and an oil. An emulsion is only stable when it cannot separate into its two component parts and this requires a third component, an emulsifying agent. Most commonly, this is a surfactant, but proteins such as casein are also good emulsifiers as they stabilise the oil-water interface through their strong adsorbed films. The form in which sizing chemicals are used at paper mills is often referred to as an emulsion, but, strictly speaking, this is only true for ASA (which is an oil) as both rosin and AKD are solids at ambient temperatures and should therefore be referred to as dispersions. Some papermaking polymers such as polyacrylamides are prepared by an emulsion polymerisation process and the liquid product used at mills is therefore a water-in-oil emulsion.

Energy

This is defined as the ability to do work, the basic measurement unit for which is the Joule.

Some useful conversion factors are:

1 Joule = 1 Newton.metre = 1 volt.coulomb = 1 watt.second = 0.00000028 kWh = 0.239 Calories

Within thermodynamics, there are several different energy expressions such as the internal energy of a system, the free energy, etc and, within papermaking, energy consumption in the various parts of the process is a very important operational parameter. From a chemistry standpoint, the energy dissipated in the wet end water system and the resultant rise in temperature is the most important practical aspect related to energy use as this has a major influence on the rate of most chemical and microbiological processes.

Enthalpy

This is a thermodynamic term, which is defined as H in the equation:

$H = E + PV$ where E = the system's internal energy, P = pressure and V = volume

At constant pressure (isobaric conditions), a change in enthalpy (ΔH) corresponds to the change in the heat content of a system. An exothermic reaction or interaction is one where heat is generated (the temperature rises) and, by convention, ΔH is negative (ie the system loses energy in order to maintain a constant temperature). An endothermic reaction or interaction is one where heat is consumed (the temperature falls) and, by convention, ΔH is positive (ie the system gains energy in order to maintain a constant temperature). Exothermic changes are thus promoted by low temperatures and endothermic changes by high temperatures. Changes in enthalpy (and entropy) determine the overall change in free energy under constant temperature conditions.

Entrained gases

All gases have a certain water solubility in accordance with Henry's Law, which means that the dissolved concentrations vary with both pressure and temperature. Dissolved gases may cause problems, albeit not the same ones as entrained gases, but they can also move from the dissolved to the insoluble (entrained) state when the temperature increases or the pressure decreases. Gases entrained at the papermaking wet end exist in a wide range of bubble sizes from above 1 mm down to about 10 microns, the smaller colloidal-sized bubbles being stabilised by surface-active agents. This stabilisation of small bubbles prevents their aggregation into larger bubbles that can more easily escape to the surface. Even then, bubbles can be mechanically trapped by the fibrous matrix despite the latter's normal hydrophilic character.

Entrained gases can be present at concentrations up to 4-5% v/v at the machine flowbox, but even levels above 0.5% v/v can cause problems such as foam, poor drainage (see example here) and poor formation quality of the paper. At these levels, the volume proportion of gas in the stock is about the same as or higher than pulp in the thin stock, so drainage and formation problems are hardly surprising. In papermaking, there are two main sources of dissolved and entrained gases:

- ❑ air from leaking pumps, tank filling, drainage on the wire, etc.
  At 30^{o}C in contact with air at atmospheric pressure, the saturation concentrations of oxygen, nitrogen and carbon dioxide correspond to dissolved gas contents by volume of about 0.5%, 1% and 0.02% respectively.
- ❑ carbon dioxide from microbial activity and chemical interactions
  The dissolution of just 100 mg/l of calcium carbonate would generate a carbon dioxide content of about 2.2% v/v if it was all retained in the stock.

Minimising the problems from entrained gases is achieved by either mechanical or chemically-assisted degassing. Entrained gases can be measured either off-line or on-line by a number of methods:

- ❑ measurement of density of sample before and after degassing (Tappi laboratory method).
- ❑ use of the variation of liquid compressibility with its gas content. There are various off-line and on-line commercial testers (eg BTG Mutek) using this principle which measures the sample volume or density at different pressures.
- ❑ ultrasonic technique (eg on-line Sonica) due to the strong signal attenuation by gas bubbles.

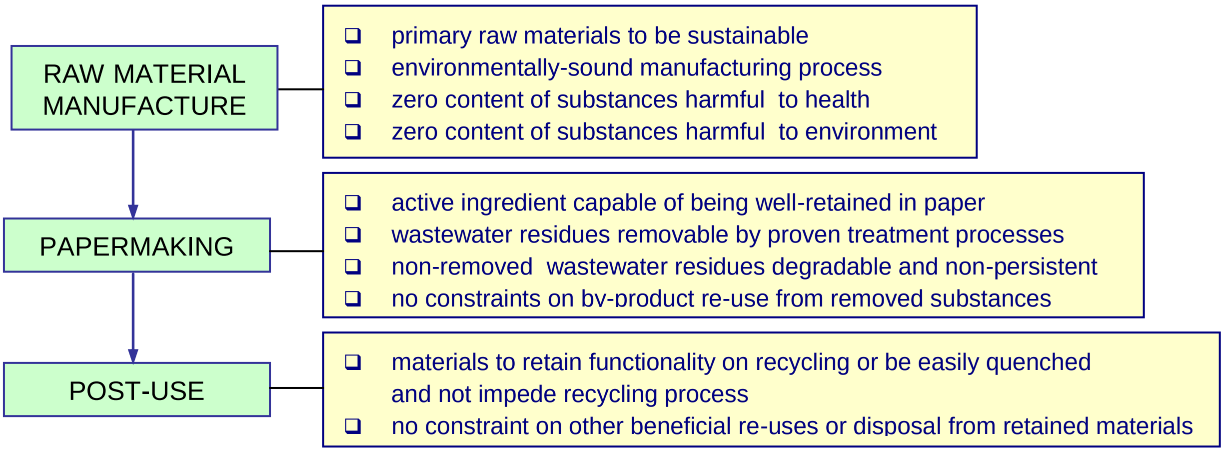
Entropy

This is defined by the second law of thermodynamics. Its most common definition is as a measure of the degree of disorder or randomness in a system. For a natural process, the entropy can only increase. In accordance with the third law of thermodynamics, the entropy of all pure, crystalline substances is zero (ie maximum order) at 0^{o}K. Changes in entropy (and enthalpy) determine the overall change in free energy under constant temperature conditions.

Environmental aspects

Since the mid-1980s, the environmental performance of the paper industry has been very much in the public domain, but the key issues have spread from the initial controversy over chlorine bleaching of pulps to cover many other facets of pulp and paper production, eg recycling, forest management, etc. The focus on the environmental profile of non-fibrous raw materials is still nothing like as strong as that on wood and pulps, but there are substantial, albeit different, concerns such as biodegradability and the environmental persistence of residual emissions. It is generally accepted today that the environmental effects stemming from the use of paper raw materials has to be considered over the whole life cycle of paper products. This raises many questions about the actual and potential impact of materials as the primary raw materials are extracted, processed into intermediates, incorporated into paper and the paper finally recycled or disposed of after use.

Having considered all these potential effects, it is possible to construct a broad, generic specification for an ideal papermaking raw material, as indicated below.



- ❑ primary raw materials to be sustainable
- ❑ environmentally-sound manufacturing process
- ❑ zero content of substances harmful to health
- ❑ zero content of substances harmful to environment

- ❑ active ingredient capable of being well-retained in paper
- ❑ wastewater residues removable by proven treatment processes
- ❑ non-removed wastewater residues degradable and non-persistent
- ❑ no constraints on by-product re-use from removed substances

- ❑ materials to retain functionality on recycling or be easily quenched and not impede recycling process
- ❑ no constraint on other beneficial re-uses or disposal from retained materials

In the papermaking stage, the key objective is that all raw materials with functionality in the product should be retained in the paper to the highest possible extent, ie maximum total retention and minimal losses to the water system. Additives that are functional within the paper making system (eg process control additives) should ideally not be retained in the paper, but remain within the machine water system. Both aims are achieved by operating machine water systems as closed as is practicable, bearing in mind the environmental consequences of producing broke when severe problems occur and the dangers of odours and other emissions to air that can occur on some machines with very closed water systems. Given the practical impossibility of achieving 100% total retention, all raw materials should be thoroughly evaluated prior to use in terms of their environmental effects outside the mill in paper products and discharges of water, wastes and possible by-products.

Enzyme-converted starches

These starches are alternatives to thermo-chemically converted starches and are produced by post-treatment of jet-cooked starches with a suitable starch-degrading enzyme. This enzyme is an α-amylase, preferably a heat-tolerant variety so that the treatment can be carried out at high temperature (about 80°C) directly after cooking the starch at high solids content. The presence of calcium ions (ie water hardness) improves the enzyme's heat tolerance. Because of the random way in which this enzyme attacks starches, enzymatically-converted starches have a with somewhat higher levels of low molecular weight starch fragments than do thermo-chemically converted starches (see this figure). After conversion, the enzyme has to be inactivated and this is normally done by raising the temperature to about 95°C for a few seconds.

Enzymes

An enzyme is a biological catalyst in the form of a protein that facilitates a specific biochemical reaction. Enzymes are usually named after one of the chemicals in the reaction that they catalyse and always end in the letters - ase. There are many different enzymes in most life forms and many occur naturally in papermaking systems as a result of the presence of micro-organisms, eg the group of amylases responsible for starch degradation and catalase that breaks down hydrogen peroxide. Enzymes contain two domains within their complex folded structures - a domain that is responsible for carrying out that particular action and a binding domain that keys the enzyme into its substrate.

Enzymes have been used in papermaking for many years, but the applications were very limited until fairly recently. The most long-standing application is probably in the enzymatic conversion of starches, which uses an α-amylase enzyme. Other enzyme applications that have been developed are:

- ❑ for control of slime problems
  This approach is based on the use of enzymes that are able to break down the extra-cellular polysaccharides that help micro-organisms stick together in slime deposits. Developments in this area go back to the early 1980s, when an enzyme-based product was marketed by one company as a replacement for biocides. This product had limited success, which was attributed to the fact that the product only contained one enzyme and was consequently only able to break down one type of polysaccharide (fructose-based levans).

  Since then, other companies (Hercules, Buckman) have been working to harness enzymes for slime control with more success. In some paper mill trials, enzyme addition can eliminate the addition of biocide to the short recirculation loop and reduce the biocide dose added to the broke. Enzyme-based systems have coped well with a change from acid to neutral pH operation with no overall change in slime control costs. At a wood-free paper mill using rosin sizing at neutral pH, enzyme treatment has been successful in controlling microbial levels and slime spots in the paper, but the cost of the enzyme-based regime was over twice that of the biocide control system (about $9/tonne compared to about $4/tonne paper). Biocide use was eliminated in the short recirculation, but was still needed for treatment of the whitewater storage tanks and saveall.

- ❑ for control of pitch
  This approach has been applied on a limited number of paper machines, mainly in Japan. It uses lipase enzymes which are able to hydrolyse the fatty acid esters within the pulp's extractives fraction. Japanese work with a groundwood newsprint furnish succeeded in reducing pitch deposits, pitch holes in the sheet and the quantity of talc used for pitch control.

- ❑ for control of stickies
  This is one of the latest application of enzymes in papermaking and has been developed by one company, Buckman. This enzyme is an esterase (an enzyme able to break down the ester linkage), for which there are at least two potential substrates within stickies - polyvinyl acetate and ethylvinyl acetate.

- ❑ as drainage aids for improving water removal
  This application mainly uses cellulase enzymes, which are able to remove (dissolve) some of the more water-retentive parts of the pulp fibre/fines by a "peeling" action. The disadvantage of this may be an increase in dissolved organics and some loss of overall pulp retention.

- ❑ for control of anionic trash
  Only one form of anionic trash has so far been successfully dealt with by enzymes and this is the pectin substances in bleached mechanical pulps. In one quoted example for a peroxide-bleached spruce TMP, treatment with a pectinase enzyme lowered the cationic demand by about 50%.

- ❑ for general machine cleaning
  The problem with using enzymes in this area is their specificity, which means that the composition of the accumulated debris needs to be known beforehand. One area where this is possible without the need for too much preliminary analytical work is the starch preparation/dosing equipment. The use of starch-degrading enzymes for this application has been pioneered by Buckman.

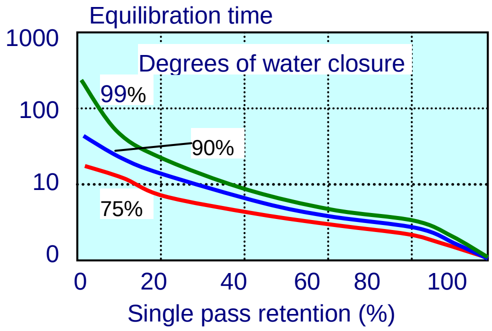
Equilibration time

In papermaking terms, this can be defined as the time for the system to come to equilibrium or steady state in terms of all the parameters that impact on product quality and process runnability. This is discussed below in relation to the wet end, but similar issues arise also within surface application systems at the size press and coaters. Equilibration time can be estimated using a simple completely-mixed model of the papermaking system, whereby it can be shown that:

Time taken to get to within X% of equilibrium value = $\log(1-X)/\log(f.[1-r])$

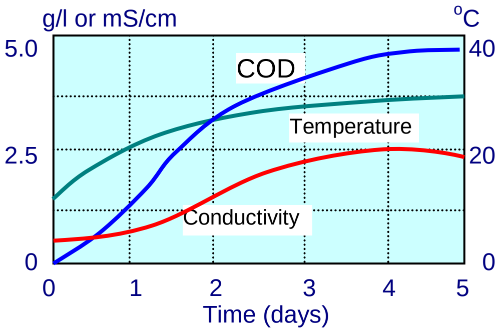
where X = proportion of equilibrium value to be calculated (fraction)
f = degree of closure (fraction) and r = single pass retention (fraction)

The model does not calculate the time taken to get to actual equilibrium value as this is infinite for an ideal completely-mixed system, so the results illustrated below indicate the time taken to get to 99% of the equilibrium value. The single pass retention (SPR) is assumed to remain constant over the equilibration time, but this may not be case due to the build-up of dissolved solids (eg anionic trash) that could adversely affect the efficacy of retention aids. It is worth noting that, even if the fines SPR does remain constant, the SPR of the total particulate matrix at start-up (its first pass retention) will not be the same as its SPR at equilibrium.



It clear that from the figure at right that variations in water use have their greatest impact on the time taken for the poorly-retained soluble fraction, but have little effect on the time taken for the well-retained fibre fraction. The product quality will change steadily in chemical terms as the system comes to equilibrium and the content of solids that were dissolved at the wet end increase to the equilibrium level. As most of these solids should be non-functional substances which dissolve incidentally at the wet end, it might be expected that the product will assume a constant quality in terms of, for example, strength and sizing well before the dissolved solids come to equilibrium. However, if the dissolved solids load is high and the system very closed, then the equilibrium product quality may be inferior to that during the equilibration phase. In terms of process runnability, which is more severely affected by wet end concentrations than is the product, the equilibrium conditions are almost certain to be the most problematic.

Clearly, the equilibration time is quite important to machines on start-up after a shutdown or a grade change. For machines making small orders, the frequency of changes is itself a constraint on closing up, which is probably quite fortunate otherwise the time taken to reach the product specification would be a substantial proportion of the total running time. Some data from start-up with fresh water is shown here for a machine making recycled liner/fluting. The relatively long time to reach a steady-state is due to all the three parameters being associated with the liquid phase (ie the left-hand side of the previous figure) and the high degree of water closure (total fresh water use about 5 m^3/tonne).



Equilibrium constants

Whenever we consider a chemical interaction between various materials, there is an equilibrium condition corresponding to when the interaction is complete. The equilibrium constant describes the relative concentrations of the reactants and products at equilibrium, but it gives no information about the rate of progress towards that conclusion (ie on its kinetics). The interaction may refer to a chemical reaction between various substances, a substance dissolving in water, a substance adsorbing on a surface, etc. For a chemical reaction:

$$A + B \rightarrow C + D$$

Equilibrium constant , $K = [A][B]/[C][D]$
where [X] represents concentration or activity of X

All equilibrium constants (K) vary with temperature (T) as follows:

$$\ln K = -\Delta G^o/RT = -\Delta H^o/RT + \Delta S^o/R$$

which on integration, $\ln \frac{K_2}{K_1} = \frac{\Delta H^o}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

where G^o = Gibb's free energy under standard conditions
H^o = enthalpy and S^o = entropy under standard conditions and R = gas constant

An increase in temperature ($T_2 > T_1$), only leads to an increase in the constant (ie an increased solubility in the case of the solubility product) where the enthalpy change is positive, ie the reaction being described is endothermic.

ESD

This is an abbreviation for the equivalent spherical diameter, which is the diameter that an anisometric particle with the same settling velocity would have if it were a sphere. It is important in relation to the characteristics of some particulate materials in papermaking, eg clays and fibres.

Ester

This is the name for the compound formed when an acid (most commonly a carboxylic acid) reacts with an alcohol as follows:

$$R_1CO_2H + R_2OH \rightarrow R_1CO_2R_2 + H_2O$$

Ester groups are present in various materials used in papermaking and sometimes present in the product as a result of curing reactions in the drying section:

- the extractives fraction of wood and possibly in pitch present in virgin pulps
- the linkages between:
  - ASA size and cellulose
  - possibly AKD size and cellulose
  - PAE resins and pulp carboxyls
- in some papermaking additives:
  - rosin esters for sizing at neutral pH
  - acrylate esters as latices in coating
  - polyvinyl acetate latices used as coating binders
  - fatty acid esters used as release agents and defoamers
  - starch esters used for surface application
  - waxes for barrier coating.

Ethers

Ethers are organic compounds containing the C - O - C linkage. The simple ethers are compounds such as diethyl ether (H_5C_2 - O - C_2H_5), but ether linkages are also present in some papermaking chemicals:

- starch ethers used as dry strength additives at the size press
- polyethylene oxide used as a retention aid
- polyethylene glycols used for foam control and as lubricants.

Ethylene vinyl acetate (EVA)

This is a co-polymer between ethylene and vinyl acetate, which can be used as a latex in paper coating. It can also enter papermaking systems in recovered paper through its use as a converting adhesive.

Eucalypts

This is a type of hardwood tree grown extensively in Australia (where it is indigenous), the Iberian peninsula and in South America (particularly in Brazil) for conversion to a papermaking pulp, mainly in the form of a bleached chemical (Kraft) pulp. They are commonly referred to as gum trees and there are many different species (ca 700), but the three grown commercially as pulp wood are:

- E.globulus (Tasmanian Blue Gum), mainly in Australia and Spain/Portugal
- E.grandis (Rose gum) and E.urophylla (Timor Gum), mainly in Brazil as individual species or as a hybrid (E.urograndis).

Eucalypt fibres are short (about 1mm in length) and slender (diameter 15-20 µm) with a relatively thick fibre wall giving a low coarseness. There are differences between some Eucalypt species in terms of coarseness, which may be important in relation to their effect on paper bulk and porosity. Generally however, eucalypt pulps are very useful in all papers where formation, surface smoothness, bulk, stiffness and softness are important.

Data in this table indicates that the content of anionic substances in one ECF bleached eucalyptus pulp (60-100 µeq/g) is comparable with that in other hardwood pulps such as birch.

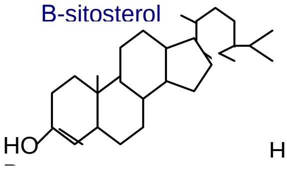
Extensive

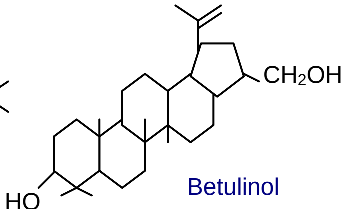
This word has a specific meaning in thermodynamics when referring to different properties of the system. An extensive property is one that depends on the mass of substance in the system, whilst an intensive property is independent of the mass of substance in the system. For example, the titrated charge demand depends on the quantity of charged substances in the sample that are accessible to the titrating chemical and is thus an extensive property. By contrast, the potential of a particle is an intensive property because the value does not depend on the number of particles present.

Extractives

This is the name for the minor fraction of wood that protects it from biological attack. The name is simply derived from the fact that the substances within this fraction are not water-soluble, but can be extracted by suitable organics solvents such as ether or dichloromethane. The extractives comprise a wide range of substances classified into several fractions:

- ❑ the terpenoids such as α- and β-pinene. They are not water soluble, but are recoverable during pulping as a by-product for use as a fuel or chemical feedstock. The resin acids are also part of this fraction, but are soluble by saponification and are thus removed from the pulp during alkaline pulping processes. They form the main part of the tall oil fraction removed during Kraft pulping of softwoods, but are not present in hardwoods.
- ❑ fatty acids (eg linoleic) in the form of fats as triglyceride esters and in the form of waxes as esters of higher fatty and terpene alcohols. Levels are higher in hardwoods (ca 1%) than softwoods (ca 0.5%).
- ❑ other compounds such as sterols and phenolics, two examples being shown at right.


B-sitosterol


Betulinol

There are considerable differences in the extractives content of different wood species and within a species depending on tree age, its growth rate and growth conditions. Softwoods (notably pines) have higher levels (typically 2-5%) than hardwoods (typically 1-2%). The extractives content varies quite widely within a single tree due to differences between the contents of the heartwood and sapwood, eg in the case of pine, the heartwood contains about twice as much as the sapwood. Although a minor fraction of the wood, extractives can cause problems on the paper machine as pitch if not removed from the wood during pulping.

FAS

This is an abbreviation for formadine-sulphinic acid.

Fastness

This term is used to describe the stability or resistance of a particular paper or chemical to an effect that is usually deleterious. It is largely used in relation to dyes and brighteners in the following three areas:

- light-fastness in relation to the resistance of the solution or treated paper to some deterioration in its colour characteristics through exposure to light.
- bleed-fastness in relation to the resistance of the colour to extraction with various liquids such as water, alcohols, etc. This is particularly important in heavily-coloured grades used as tissue and towel. The use of fixatives can help bleed-fastness.
- heat-fastness in relation to loss of colour when exposed to a heat source such as during paper drying, which can lead to migration and impaired colour uniformity.

Fatty acids

This is the common term for the series of saturated monocarboxylic acids (formula below) starting with formic acid (HCOOH) and they are the main type of organic acids found in papermaking systems. The name is derived from that the fact that some of the higher members, notably palmitic and stearic acids (see below), occur in natural fats as their glyceride esters. The lower members such as acetic and propionic are usually referred to as volatile fatty acids (VFAs). Unsaturated monocarboxylic acids (see formula below) such as oleic acid can also be referred to as fatty acids. High esters of the higher fatty acids are referred to as waxes.

Saturated acids - $C_nH_{2n+1}COOH$	VFAs HCOOH - formic acid	Unsaturated acids $C_nH_{2n-1}COOH$
$C_{15}H_{31}COOH$ - Palmitic acid	CH_3COOH - acetic acid	$C_{15}H_{29}COOH$ - oleic acid
$C_{17}H_{35}COOH$ - Stearic acid	C_2H_5COOH - propionic acid	$C_{17}H_{33}COOH$ - linoleic acid

Fatty acids may be present in papermaking from various sources:

- wood contains the unsaturated linoleic acid (see above) in the extractives fraction
- AKD sizes are made from saturated acids and the alkenyl version from unsaturated fatty acids
- volatile fatty acids such as acetic acid, propionic acid and butyric acid are generated by anaerobic acid-producing bacteria within the papermaking process
- higher fatty acids are added to enhance ink removal in flotation and which could (although unlikely given the position of the flotation stage) be carried over with the pulp to the paper machine
- as calcium stearate which is used as a coating lubricant.

FBA

This is an abbreviation for fluorescent brightening agent.

Fermentation

This is the process of bio-oxidation whereby an organic substrate, typically a carbohydrate, is partially used for oxidation and partially for reduction. The typical products of such fermentations are organic acids such as acetic, propionic, lactic, etc. Fermentations are carried out by facultative aerobic bacteria such as Clostridia species. Such fermentations are not uncommon in papermaking systems, notably at recycled mills with fairly closed water systems where the levels of dissolved organics (notably starches) are typically several 1000 mg/l (as COD) and may reach several 10,000 mg/l in fully closed water systems. This leads to relatively low or zero levels of dissolved oxygen saturation, which are ideal conditions for growth of fermentative bacteria. Control of such bacteria is an important element in the overall control of microbiological problems.

Fibre

Although this term does have a precise meaning, it tends to be used somewhat indiscriminately in papermaking and is often used in the same sense as the whole pulp. Strictly speaking, true fibres are the dominant cells only in hardwood pulps as tracheid is the more correct term for the dominant fraction in softwood pulps.

In a slightly different sense, the term "fibre fraction" or sometimes just "fibre" is often used in papermaking to denote that part of the pulp that is not fines, ie is retained on the standard 200 mesh wire used in the normal test for fines content. In this document, this last definition will be used and the term "pulp" used to denote the whole of the fibrous raw material that enters the papermaking system. Genuine fibres form the strong backbone of all paper products and therefore always play an important role in papermaking chemistry. The basic fibrous quality of all pulps and hence of all papers is due to the cellulose content of the pulps used, but the contents of the other main components (lignin, hemicelluloses and extractives) also play an important, albeit less positive, role.

There are three fundamental physical properties of pulp fibres:

- fibre length

  This is a major contributor to the strength of pulps and is usually measured in mm. For wood pulps, fibre length varies from about 1mm for hardwoods to 4mm for softwoods. For any wood species, fibre length increases with age of the tree up to about 30 years for hardwoods and 40 years for softwoods, but remains constant thereafter. The length of some non-wood fibres can be much greater than these values.

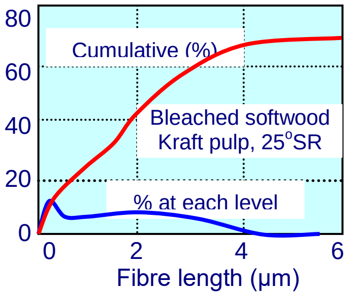
- fibre diameter

  This is usually measured in microns (µm) and varies from about 20 µm for hardwoods to about 50µm for softwoods.

- fibre wall thickness

  This is usually measured in microns (µm) and varies from about 3µm for birch to around 10µm for pine.

A useful parameter which depends on the balance of the above dimensions and on the fibre density is the fibre coarseness, which is measured in mg/m fibre length. Within each papermaking pulp (particularly after refining), there will be a wide distribution of fibre lengths and this can be quantified by the traditional Bauer-McNett classifier or by automated fibre length analysers (see example at right using a Kajaani FS-200 analyser for the fines-free fraction of the refined pulp having a length-weighted mean fibre length of 2.6 µm). Further data on the effect of process chemistry on the size of fibre aggregates for this pulp is given under flocculation and for the effect of a formation aid under that heading.



Source: Beghello in J Pulp Paper Science, 1998, 13, 4, 274-279.

Fibre saturation point (FSP)

This parameter is a measure of a pulp's ability to swell and is an alternative technique to measurement of its water retention value. Both parameters have the units of g water/g dry pulp. The FSP measurement is based on the technique of inverse solute (or size) exclusion chromatography, in which a polymer of a certain size (normally a dextran with a molecular mass of 2M Daltons) is added to the pulp sample at a precisely known consistency. The polymer solution is diluted by the water content of the pulp, the degree of dilution depending on how much water is accessible to the polymer. Not all the water in the sample is accessible to this polymer as it is larger than some of the pores in the fibre wall. The level of non-accessible water within the fibre wall can thus be calculated by simply measuring the polymer concentration, which depends on the swollen state of the pulp.

The FSP value is usually lower than the WRV as shown in the following table (see more data from this study under drying). Essentially, the water measured as the FSP is a mixture of the unbound water within macropores and the bound water within micropores of the fibre wall, whereas the WRV includes some bulk water (see water removal for description of different types of water).

Sample	WRV (g/g)	FSP (g/g)	Non-freezing water (g/g)	Freeness (^{o}SR)
Dried UBK	1.23	0.88	0.35	14
Never-dried UBK	1.41	1.13	0.37	14
Never-dried UBK refined	1.93	1.56	0.38	27
Never-dried UBK + 10% fines	2.35	1.58	0.39	71

Source: Maloney et al in Paper Technology, 1998, 39, 6, 39-47.

Other examples with FSP data are shown here for a chemimechanical pulp in terms of its anionic group content.

Fibrils

This is the name given to the hydrogen-bonded associations of cellulose molecules present in raw fibres (both wood and non-wood) and in papermaking pulps. Individual fibrils can be classified in terms of their size into the following types (but note that this terminology is not universally applied):

- ☐ proto- or elementary fibrils, which have a rectangular cross-section measuring about 3x7 nm
- ☐ micro-fibrils, which are about 25 nm in diameter
- ☐ macro-fibrils, which are about 0.5 microns (500 nm) in diameter.

Fillers

The term "filler" implies that this set of materials is simply present to make up as much of the paper weight as possible and thus reduce its specific cost. Although some fillers do lower the furnish cost, this is not the main reason for their use and a better term for this set of materials would be "opacifiers" as this is their main, but again not only, role as wet end additives. The same chemical types are also used, albeit in a slightly different physical form, for paper coating, when the term "pigment" is more commonly used to describe them. The two terms (filler and pigment) are often used interchangeably in papermaking, but, in this document, the term filler (despite its economic implications) will be used for wet end applied materials and pigments for coating materials.

However, wet end fillers need to be differentiated on price grounds into two groups:

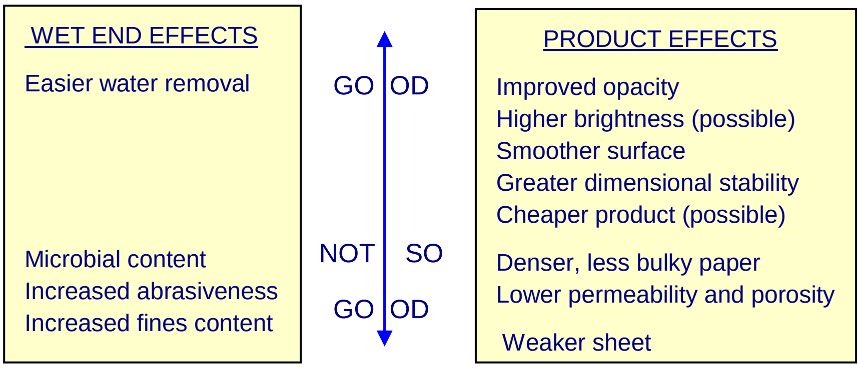
- the general-purpose, low-cost fillers such as kaolin clay, calcium carbonate and talc
- minerals such as titanium dioxide, for which the term "filler" is somewhat inappropriate as they are more expensive than the highest-price pulps.

The use of fillers (and pigments) in papermaking has increased ahead of the general growth in paper production due to rising filler contents and high growth in those grades using fillers (and pigments). Across the whole paper industry, fillers and pigments are collectively the highest-tonnage non-fibrous raw material, global consumption being about 25M tonne p.a. However, their use is predominantly in one sector, printings/writing grades, where uncoated grades may contain up to about 35% filler and coated grades may have a total mineral content as high as 50%.

Within the filler market, there have been tremendous changes over the last 20 years with much greater use of calcium carbonates in place of both kaolin clays and titanium dioxide, particularly in the wood-free sector. This has been possible largely due to the ability to make papers under neutral/alkaline pH conditions, which is desirable, if not essential, in order to make effective use of calcium carbonate. Previously, the sized wood-free grades would have been made predominantly with kaolin clay under the acidic conditions (ca pH 5) required for the most effective use of the then normal sizing chemical, rosin. The change to neutral/alkaline conditions for making wood-free papers has been made possible by the development of sizing systems that are sometimes still based on rosin, but more commonly on other sizing chemicals, mainly AKD and ASA, that function well at neutral pH.

This sizing factor is not present in the wood-containing paper sector, where the move away from clay filler to calcium carbonate took place later (and is still taking place), but learning how to make these grades at a higher wet end pH was still a major factor in the successful transition from acid to neutral papermaking. Key factors in this sector were achieving good runnability at neutral pH, where pitch was likely to be a greater problem than at acid pH and also maintaining acceptable brightness in the face of the darkening effect of higher pH on the residual lignin in mechanical pulps. In both sectors, it is important to recognise that these changes in filler use have profound effects on wet end chemistry, not simply due to the changed physical and chemical properties of the filler, but also due to the changes in the chemistry of other additives (eg no or less alum) and the higher operating pH with calcium carbonates.

The effects of fillers within the papermaking process are summarised very broadly in the figure below, the main positive reasons for using fillers being the improvement in the optical and surface properties of the formed sheet, ie opacity, smoothness and possibly brightness.



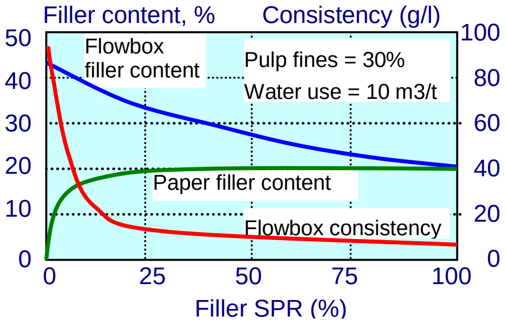
The improvement in the ease of water removal is useful, but never a driving force in itself for increasing the filler content due to the accompanying constraints of lower strength and bulk plus the range of wet end problems that can arise due to the raised fines content. The effect of fillers on the optical characteristics of paper is usually central to their use and the interaction between light and a paper surface is described here. The important characteristics of fillers are their refractive index, brightness, particle size distribution (in terms of specific particle numbers and surface area), particle morphology and density. The light scattering coefficient of the filler is determined by a combination of refractive index and particle morphology and is the most important property determining the fillers' contribution to paper opacity. The properties of fillers that are important in terms of wet end chemistry are somewhat different to the functional ones expressed once they are in the paper. Some of these properties are filler-specific and will be covered under each material, but some are generic and are summarised below.

As is evident from the above figure, the effects of filler use on wet end chemistry are generally unwelcome. The one clear exception is the improvement in the ease of water removal brought about by the low water-holding capacity of fillers compared to hydrophilic fibres. This is an important attribute as it allows the paper machine to be operated at faster speeds as the filler content increases, but only provided that other changes that may accompany filler use (eg increased pulp refining and/or greater use of wet end starches to compensate for the impaired paper strength) do not outweigh this effect. All fillers have the ability to ease water removal, but there are differences between the various fillers depending on the filler’s shape. For example, fillers such as clay tend to be aligned with a horizontal plate surface and this impedes the passage of water simply by imposing a rather tortuous path for the water to follow. Improved water removal is thus another of the benefits to be gained in changing to the more regular-shaped calcium carbonate filler.

The abrasion characteristics of fillers are related to their hardness, but may in practice be more due to the hardness of impurities than of the main filler material. Excessive wear of materials through abrasion may occur at the wet end (eg wires) and during conversion (eg slitters and cutters). Although not self-evident from their mineral nature, it should be noted that natural fillers can contain a significant microbial load (see this figure), but the level in slurry products is more controllable as a biocide is usually incorporated.

However, the main problems caused by wet end fillers arise from their small particle size and consequent high particle numbers and surface area. These effects are experienced in four main areas:

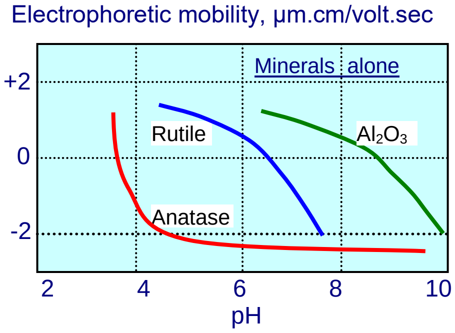
- the single pass retention characteristics of the particulate matrix gets worse through the increasing number of fine particles
- the higher surface area at the wet end increases the potential for adsorption of water-soluble additives
- the higher surface area in the final product increases the demand for any chemicals that require full surface coverage for their effect, eg sizing agents and colorants
- the paper strength declines due to physical interference with inter-fibre bonding, which is usually compensated for by the use of dry strength agents.



Filler retention (both single pass and total) is of obvious importance and this means that the use of fillers, being part of the fines fraction, is always accompanied by the use of retention aids. As illustrated in the figure at right (derived from a model of the papermaking system), the single pass filler retention (SPR) should be maintained at as high level as possible in order to minimise flowbox consistency and flowbox filler content. Under the flow conditions in this particular example, the flowbox consistency reaches unrealistic levels (above 10 g/l) that would give increasingly poor paper (formation) quality when the filler SPR declines below about 25%. A similar trend was shown here for pulp fines.

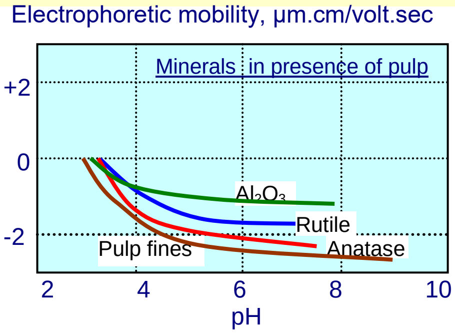
The variables that affect filler retention are the same as for fine particles generally, being dependent on their state of aggregation with the rest of the particulate matrix, which is itself dependent on many other variables. The physical form of the fibre surface depends on the extent of fibrillation that occurs during refining. In the absence of retention aids, increased refining of the pulp improves filler retention through enhanced filler deposition, but any dependence of retention on particle size is effectively removed when retention aids are used. Examples of these effects are shown here for clay filler.

The surface chemistry of the fillers is important as this should influence the selection of retention chemicals and other additives (eg dry strength agents). In practice, the filler's surface chemistry is less critical than might be expected and this is illustrated in the figures at right (albeit for two speciality "fillers", titanium dioxide and alumina, rather than the more common clays/carbonates). Each filler has a characteristic surface charge (expressed here as mobility rather than as a calculated zeta potential), which varies with pH to give a zero charge at the isoelectric point (upper figure).

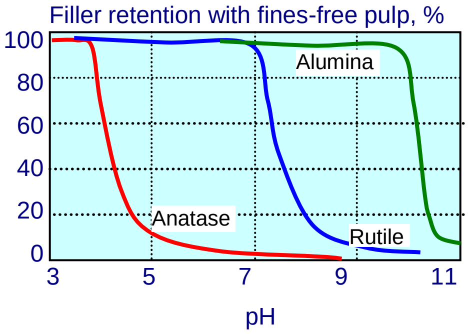


Source: Jaycock at 1st International seminar on Papermaking Chemistry, 1977, Amsterdam.

However, when the filler's mobility is measured in the presence of pulp (lower figure), the charge of all fillers becomes anionic due to the adsorption of anionic hemi-celluloses that have dissolved from the pulp. The original charge of the filler (its natural charge in "clean" water) does influence its charge in the presence of pulp and a more cationic filler (eg the aluminium oxide) tends to adsorb more pulp-derived anionic substances at any particular pH.

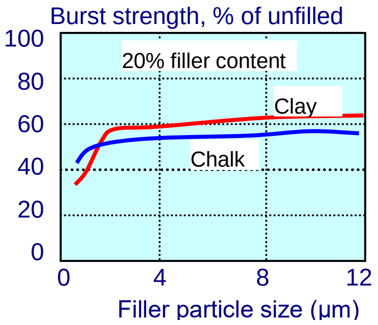


When the retention of the same fillers is measured in a low-shear laboratory system using a washed pulp, the effect of pH as shown below is obtained. When a normal (unwashed) pulp was used, the filler retention no longer showed this pattern of pH dependence, but was similar to that of the pulp fines. The artificial conditions of washing the pulp, mainly to remove pulp-derived fines, has also removed the anionic pulp hemi-celluloses responsible for the loss of filler cationicity shown above. The filler retention is thus high when the filler is cationic, as this allows good hetero-coagulation of filler and genuine fibres, but retention is lost above the fillers' iso-electric point.



The surface charge of papermaking fillers is thus very dependent on the chemistry of the surrounding liquid phase due to their tendency to adsorb ions or charged organic molecules from solution. The concept of deliberately producing a cationic wet end filler has been looked into by some filler manufacturers, but has never shown any clear advantage due partly to the above phenomenon. The one exception is the possible advantages of cationically-dispersed fillers for use as a coating pigment, but, despite some advantages related to the re-use of coated broke, there are some basic unresolved problems (lower solids content, higher viscosity) with a cationic as opposed to anionic slurry.

The loss of sheet strength is an important issue accompanying the use of fillers. As seen in the example at right, this gets worse with decreasing filler particle size due to a combination of increased particle numbers and increased surface area. This weakening effect of fine fillers (the most common type) is lessened by aggregation of the filler, but this also reduces the filler's light scattering efficiency. Controlled filler aggregation is essential in order to achieve reasonable filler retention so the light scattering of the aggregated filler determines the dose required for the specified opacity. The most common chemical for strength compensation in filled papers is starch, which, in its most common cationic form, also helps filler retention. The adsorption of cationic starch on fillers is an essential step in this process and an example of this is shown here.



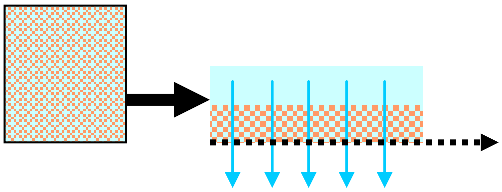
Source: Bown in Transactions 11th FRS, 1997, 83-137.

Film formation

This refers to the application of an additive to the surface of the paper, where the intention is to form a continuous film. This is relevant to paper coating, particularly where the coating is acting as a barrier and to starch addition at the size press. One of the most important properties of the applied coating is its minimum film formation temperature, which depends on its glass transition temperature, particle size and degree of cross-linking.

Filtration

Filtration is part of the overall process of water removal that starts with the drainage stage once the papermaking stock is released from the flowbox. In filtration, water removal takes place at the interface between the suspension and the formation wire with a sharp change in consistency between the mat and the overlying suspension (as shown in the picture at right). In papermaking, filtration increases the consistency from somewhere in the normal range 1 to 10 g/l (0.1 to 1%) at the flowbox to 3-5% and is then followed by a thickening stage. Filtration tends to be associated with a degree of two-sidedness in the paper as any free fine particles are intercepted and retained at the paper solid-liquid interface. This can be minimised by forming paper at the highest possible consistency and by the use of retention/drainage aids to aggregate the fines with the rest of the particulate matrix.



Fines

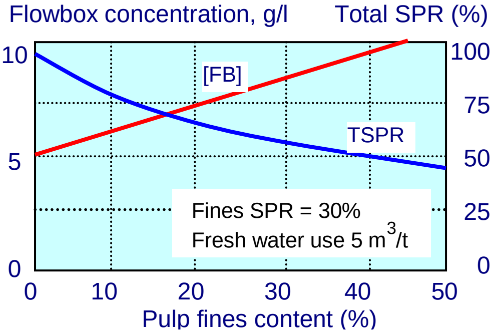
This is a very important fraction of the particulate matrix at the wet end and is defined as particles that pass through a 200 mesh sieve as measured using the Dynamic Drainage Jar (Tappi test method T261). The fines fraction of a pulp can also be determined as part of the Bauer-McNett classification of pulp solids using a 200 mesh size for the final screen. The mesh openings in a 200 mesh screen have a side length of 76 µm, but the diameter of the openings is about 107 µm. It should be noted that fines measured by optical fibre length analysers usually under-estimate the fines content significantly.

The fines fraction (as % of total particulate solids) is very important in relation to wet end chemistry as it determines the retention and drainage characteristics of the furnish and in relation to paper quality through its effect on bonding and sheet packing. The term "fines" is superfluous in discussing coating raw materials at their addition point as all the particulate materials in coating are essentially fines, but this fact becomes important when coated broke is recycled as all the coating solids then contribute to the level of wet end fines.

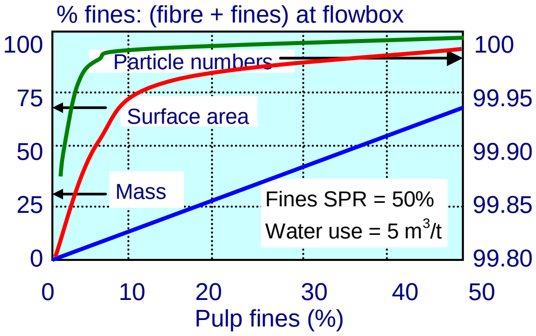
As is evident from the range of particle sizes present in papermaking raw materials, particulate fines include three important sets of wet end substances:

- ☐ the fines fraction of pulps, there being three different sorts of pulp fines:
  - primary fines which are the natural fines present in the raw, unrefined pulp
  - secondary fines which are the additional fines generated during refining
  - tertiary fines which are those generated during the rest of the papermaking process.

  Primary fines are very heterogeneous as they comprise various fragments detached from wood particles, eg parenchyma and ray cells, vessel elements, etc. Mechanical pulps have the highest level of fines amongst virgin pulps (typically 25-35% of the pulp) and are essentially all primary fines as these pulps are not usually refined. The levels of primary fines in chemical pulps are much lower (below 10% for both softwoods and hardwoods) and contribute little to strength. However, they scatter light more effectively than do secondary fines as the latter bond more closely to the fibre surface and thus improve strength more effectively. Secondary fines are thus important on machines using chemical pulps, where refining can increase the fines content to 10-20%. The difference between the impact of primary and secondary fines of bleached Kraft pulps on sizing is shown here. Some researchers have also broken down the primary pulp fines in mechanical pulps into various fractions depending on their settling characteristics - see this example for a TMP in terms of the distribution of anionic substances.



The example at right (based on the model of the papermaking system) shows the influence of pulp fines content on the total flowbox concentration and total SPR when other parameters (notably fines single pass retention) remain constant. With this rather low fines SPR, the proportion of fines at the flowbox increases to about 80% of the total particulates when the pulp fines content reaches 45%. When the pulp fines content increases in this way (through using a different pulp or refining an existing pulp more), the flowbox concentration can only be lowered by either improving fines SPR (ie using better retention aid system) or by increasing the flowbox flow.



A more dramatic representation of the changes brought about by an increased fines content is shown at right when the flowbox data is plotted as the surface area and particle numbers as well as mass. When the pulp fines content is just 20%, about 83% of the total surface area is on the fines and 99.996% of the total particles is accounted for by pulp fines.

- all fillers added at the wet end and coating pigments recycled to the wet end in coated broke.

  The presence of fresh filler/pigment-derived fines is restricted to those machines making printing/writing papers, but many grades of recovered paper will also contain these materials. As filler contents for some papers (eg SC grades) are 30-35%, the total fines content of the filled thick stock can easily reach 50% and thus show a similar increase in flowbox concentration to that depicted above. Whereas increased pulp fines can lead to impaired drainage due to their water-holding character, filler fines tend to facilitate overall water removal (although this does vary with filler type).

- all size emulsions or dispersions.

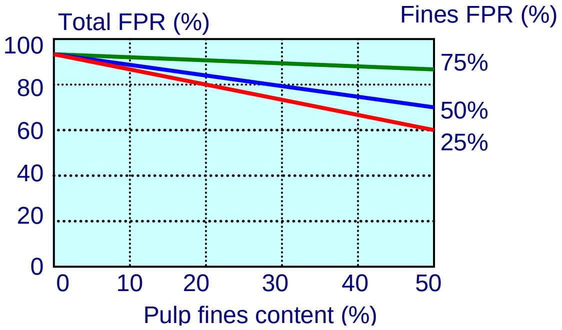
  The contribution of these materials is small in mass terms compared to the pulp fines and filler that will be present on most machines making sized grades (see this example for relationship between fines and AKD size retention).

There is one other group of substances strongly associated with the fines fraction at the wet end and this is the range of water-soluble additives (eg starch, wet strength resins, etc) that rely on being initially adsorbed on the particulate matrix in order to be retained in the product. The reason why the fines fraction plays such a key role in adsorption is simply due to their much higher specific surface area (m^2/g) compared to that of the intact fibres from pulps (see this example).

First pass retention

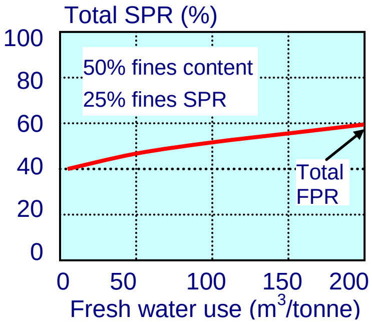
This term is often used interchangeably with single pass retention, but it is best used explicitly to refer to the single pass retention under start-up conditions, ie the very first time that the furnish passes the flowbox. At actual start-up, the composition of the thin stock at the flowbox is a more dilute version of the thick stock as there is (as yet) no whitewater for return, ie the water system is effectively open until whitewater is generated for thick stock dilution at the fan pump. The first pass retention of the total furnish is thus simply the proportional contribution from the pulp's fibre and fines fractions, as follows:

Total FPR = (Pulp fibre content x fibre FPR) + (Pulp fines content x fines FPR)



The figure at right shows the relationship between the total FPR and the fines content at three different levels of fines FPR, but with a constant fibre FPR (95%). The pulp fines content is taken up to a realistic maximum (50%), but the total FPR would obviously reach the assumed fines FPR if extended to 100% fines content. As production proceeds after start-up, whitewater is generated and returned to the fan pump, so the composition of the flowbox stock changes due to the higher contribution from the poorer-retained fines fraction compared to the better-retained (fibre) fraction.

Progress towards the steady state equilibrium is effectively the transition from an open water system to the machine's normal degree of water closure. Over the course of this period of time, the composition of the flowbox stock changes to reflect the degree of water closure at each moment. At steady state, the wet end chemistry (particularly dissolved concentrations and temperature) is different to that at start up and the SPR of the fines fraction may not be the same as their FPR. This could be due, for example, to the build-up of anionic trash, which could negate the efficacy of a cationic retention aid. Assuming for the purposes of illustration that the SPR remains at the FPR level, the total SPR can be calculated at different degrees of ultimate water closure. This is shown at left for the worst case scenario of a high pulp fines content and low fines SPR. The total FPR is 60% (same as in the first figure above) for the completely open water system (about 200 m^3/tonnne), but the total SPR under conditions of high water closure (about 4m^3/tonne) is about 40%. The equilibrium SPR is always lower than the start-up FPR due to the fines build-up.



Fixative

Originally, this term was used largely to describe the chemicals that are used to aid the adsorption of dyes on the particulate matrix, but it has since extended to cover wet end additives used to "fix" a problem such as anionic trash or pitch/stickies. Common fixatives for dyes are derivatives of dicyandiamide.

Flocculation

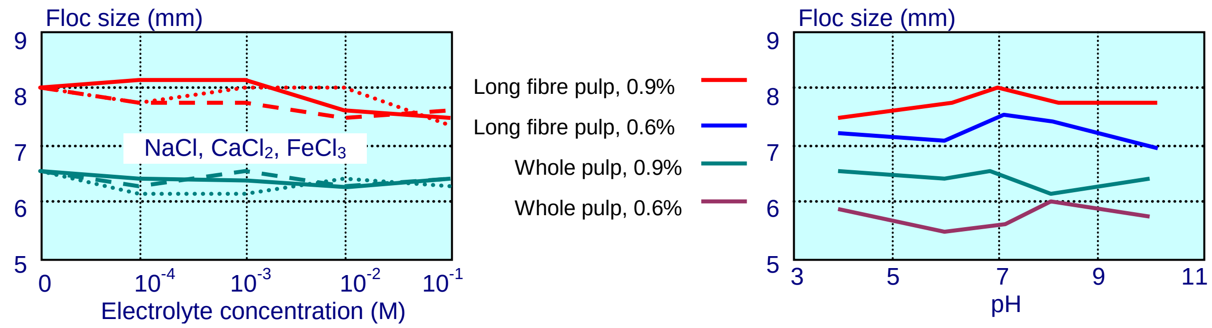
Flocculation is one of the terms used to describe the aggregation of particles in a suspension and, like the term coagulation, is often used somewhat loosely to mean aggregation brought about by any added chemical. It is also used with any one of three more specific meanings:

- for the aggregation of particles brought about by organic polymers that function by a bridging mechanism, such as polyacrylamides.
- for the aggregation of particles in the secondary minimum (whilst coagulation denotes particle aggregation in the primary minimum). This sort of aggregation is not common in papermaking due to the weakness of the net attractive force at this relatively large inter-particle distance.
- aggregation of true fibres, which is used in this sense mainly by paper physicists. In order to differentiate it from the aggregation of fines, this is sometimes referred to as macro-flocculation.

Fibre flocculation differs from fines flocculation in that it is not caused by colloidal forces such as electrostatic attraction or van der Waals forces, but by mechanical forces such as surface entanglement/linkage and by elastic fibre bending. At normal wet end consistencies, fibre flocs are continually forming, breaking down and re-forming in a form of "dynamic equilibrium". Fibres are colliding due to rotation as well as by translation of the fibres within the liquid. These non-colloidal forces are the main ones affecting paper formation, but their effect is exacerbated by the use of retention aids which cannot distinguish between intact fibres and their intended contact surface - the pulp fines and fillers. Fortunately, the much higher surface area of pulp fines and fillers ensures that the majority of added flocculants (and other additives) adsorbs on the fines fraction.

A lot of fundamental work has been conducted with the aim of using fundamental properties of fibre suspensions (such as its crowding number) to estimate the number of inter-fibre contacts in a fibre suspension and then relating this to the state of flocculation of the wet end suspension and the formation quality of the paper.

Very little work has been carried out on the effect of process chemistry on fibre flocculation, but a recent study has confirmed the intuitive thinking that changes in pH and electrolyte levels have little impact, particularly when compared to their significant effect on the aggregation of fines (see this figure). As shown in the figures below for a whole pulp (bleached softwood Kraft refined to 25°SR) and its long fibre (fines-free) fraction, any change in floc size (measured by image analysis) brought about by changes of electrolytes or pH is small compared to the effects of consistency (shown in the pH diagram at right below) and the effects of the pulp composition (as shown by the differences in both diagrams between the whole and fractionated pulps). An example of the effect of a formation aid (CMC) on fibre flocculation is shown here.



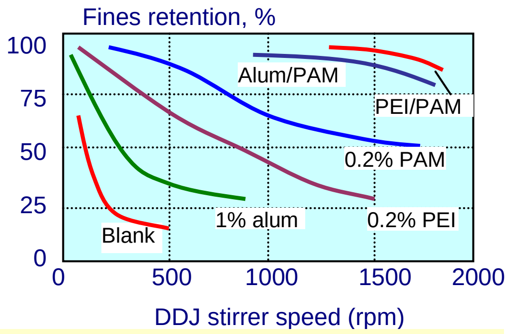
Source: Beghello in J Pulp Paper Science, 1998, 13, 4, 274-279.

Another aspect of flocculation that has received much attention over the last 10 years or so has been the development of on-line sensors to measure flocculation. Several of the now well-established consistency/retention monitoring and control systems based on various optical sensors have utilised some of the existing measurement signals to give an index of the state of flocculation of the flowbox stock. This measurement is usually based on analysis of the variability of the signal from a laser light source passing through the flowing stock. When a stock is well-flocculated with a large floc structure, the variance of the transmitted light is high compared to the much lower variance when the stock is reasonably flocculated, but with a small floc structure.

Floc strength

All aggregates of papermaking materials at the wet end can be broken down into smaller aggregates by the shear forces operating within the papermaking system. Under low shear conditions and with a suitably low surface charge and/or thin electrical double layer due to high electrolyte levels, particles can aggregate by van der Waals forces, but these aggregates have very low resistance to higher shear levels. These are sometimes referred to as "soft" flocs. Polymers give a stronger floc structure ("hard" flocs), but there is a considerable range of floc strength depending on the number of polymers being used and their mechanism in the following order of declining floc strength - dual polymers > bridging polymers > charge-patch polymers. Aggregation between oppositely-charged particles also has low resistance to shear in the absence of adsorbed polymers.

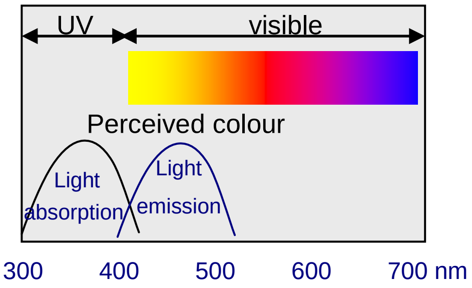
One of the simplest ways to investigate the effect of chemical treatment on floc strength uses the Dynamic Drainage Jar (DDJ) at different stirrer speeds as the shear variable. The DDJ retention is then plotted against stirrer speed as shown in the figure at left giving a retention-shear profile. This particular example corroborates the relative floc strength of alum/polymers alone and combinations thereof. Another important aspect related to floc strength is the ability of broken flocs to re-aggregate once the shear is removed or reduced and this is discussed further under re-flocculation.

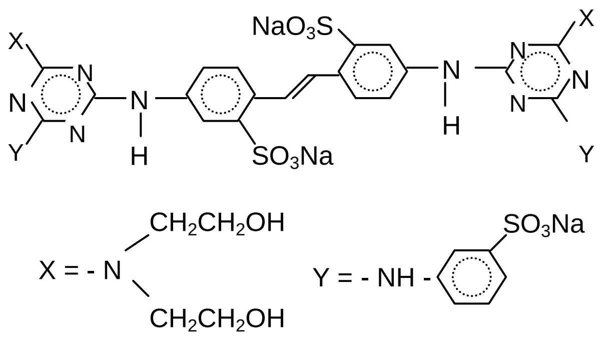


Reference: Pulp Paper Canada, 1979, 80, 6, 67-72.

Fluorescent brightening agents

These chemicals are sometimes called fluorescent whiteners or optical brighteners, but their correct name is fluorescent brighteners or brightening agents (FBAs). They function through their ability to absorb light in the near ultra-violet and re-emit the light (fluoresce) at a higher wavelength in the perceived blue region of the visible spectrum (as shown at right). This gives a slight blue cast to the paper, which is useful in overcoming the slight yellowness from residual lignin in bleached chemical pulps. Their action can be measured by the paper's whiteness or a modified brightness.





The chemistry of FBAs has some similarities to that of anionic direct dyes, but nearly all FBAs used in papermaking are triazinyl derivatives of a single chemical entity, 4,4`-diaminostilbene-2,2`-disulphonic acid (see formula at left). Other fluorescent chemistries based on coumarins and naphthalimides are available, but are much more expensive and their use is restricted to textile applications.

Fluorescence occurs because these molecules have a rigid structure, which does not permit the absorbed energy to be released by other means such as the vibrational relaxation occurring with dyes. The X group (eg diethanolamine as shown above) and the Y group (eg mono-sulphonated aniline as shown above) are selected to give the required fluorescence characteristics and the optimum balance between solubility and fibre substantivity. Electrophilic groups such as sulphonate tend to decrease fluorescence and nucleophilic groups such as hydroxyl and amino groups tend to increase it. Solutions of FBAs are sensitive to ultra-violet light, which converts the trans-isomer of stilbene to the cis-isomer form. The latter is less substantive and does not fluoresce in the available UV region. This tendency to isomerise increases with the content of electrophilic sulphonate groups, but all supplied and diluted FBA solutions need to be protected from light in order to prevent photodegradation. The light-fastness of FBA-treated papers depends on similar factors.

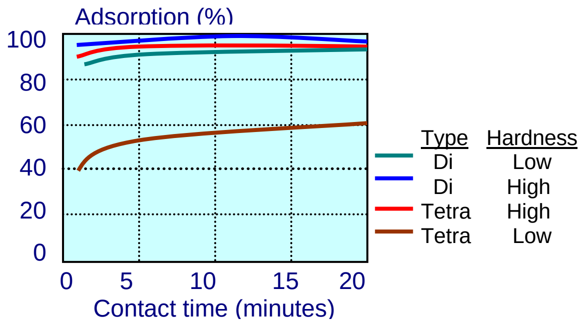
All of the stilbene-based brighteners are normally supplied as liquid products with a solids content of around 40%. Due to their anionic character, they are slightly alkaline and, like dyes, require solubilising chemicals (eg urea) to maintain solution stability in the presence of normal electrolyte levels. Products are available in urea-free forms with low electrolyte levels, but they do then suffer from higher freezing points, an important issue in terms of storage.

There is a family of stilbene-based FBAs depending on their sulphonate content:

- the di-sulphonated derivative (where the Y group is just aniline with no sulphonate groups) have the lowest water solubility (particularly under acid conditions) and are thus the most substantive to the fibre. Due to their high cost, they are only used at the wet end under certain extreme conditions such as low water hardness and high levels of cationicity.
- the tetra-sulphonated type (where each Y group contains one sulphonate group, as shown above) combine reasonable water solubility with good substantivity. Due to this combination of desirable attributes and the lowest production costs, they are the most common type of FBA (sometimes referred to as the universal FBA) and are used for all types of application.
- the hexa-sulphonated types (where the Y group contains two sulphonate groups) have the highest solubility (and brightening effect per unit mass) and lowest substantivity. Due to high cost, they are used for surface application when the highest levels of whiteness in the paper are required.

Aggregation of precipitated brightener molecules leads to a change in the emission wavelength so that the brightener gives a green rather than a blue coloration. This phenomenon, known as "greening", is caused by aggregation of the brightener molecules and may be caused by high brightener concentrations, acidity, alum or cationic materials, the latter effects also being referred to as "quenching". This problem is greatest for the di-sulphonated types due to their low solubility although they do have the advantage that, being the least anionic, they interact less with cationic chemicals. Greening is least for hexa-sulphonated brighteners which is why high levels can be used at the size press to give very high paper brightness.

At the wet end, FBAs are ineffective in the presence of other materials that absorb strongly in the ultra-violet such as titanium dioxide and mechanical pulps (due to their lignin content) and are thus mainly used with furnishes having a high content of bleached chemical pulps. For efficient retention at the wet end, the FBA should be adsorbed by the particulate matrix as individual molecules and this requires rapid adsorption in order to minimise aggregation (such as by quenching when other cationic chemicals are present). For this reason, the addition points of FBA and any strongly cationic additives should be separated as far as possible with the brightener generally being added first. For the most commonly-used tetra-sulphonated brighteners, adsorption is enhanced by the presence of hardness salts and by increased temperature and contact time. The difference in the sensitivity of di- and tetra-sulphonated brighteners to hardness is shown in the figure at right, which shows that a tetra-sulphonate in a high hardness water is better adsorbed than a di-sulphonate in a low hardness water.



Source: Murray in "Paper Chemistry", Blackie, 1995, chapter 10, 161-193.

Wet end addition of FBAs becomes less efficient as the grammage of the paper increases due to the reduced light penetration into the body of the paper. Size press addition is this more efficient at high paper grammages, but the most common way of utilising FBAs is split addition, typically about 20% addition at the wet end and 80% at the size press with total doses up to 20 kg/tonne (higher in extreme cases). Size press application can give a degree of fluorescent mottle if the FBAs are aggregated, although this is unlikely for the hexa-sulphonated brighteners and is more tolerable than the similar case of colour mottle when size press dyes are used.

Surface addition has a different set of compatibility issues than those present at the wet end, but wet end chemicals can still be leached into the size press solution and lead to quenching of the brightener. Acidity in the size press solution (from leaching or microbial activity in the starch solution) can be dealt with by the use of pH-buffered FBAs (eg with added ethanolamine) or by the direct addition of pH buffers to the size press solution. Cationic size press starches are less cationic than wet end cationic starches, but can still quench size press FBAs. FBAs are also widely used in coating formulations, but care over compatibility is again required due to the chemical complexity of some coating mixes. FBAs have little affinity for mineral particles, so it is important to use binders with good FBA affinity, eg starches, CMC or polyvinyl alcohol within the coating formulation. In both size press and coater applications, migration of less substantive FBAs to the base paper can occur leading to loss of efficacy.

At high surface addition rates, particularly of the hexa-sulphonated FBA, high levels of dissolved FBA are generated on broke recycling. This contributes to wet end cationic demand and is also undesirable due to variable FBA retention and hence variable brightening in the product. It is possible to improve the brightening of the standard tetra-sulphonated brightener, particularly its greening limit, by chemical modification so that it can replace the hexa-sulphonated FBA at the size press. Recent studies by one supplier have shown that this can reduce the cationic demand of repulped broke by about 20% and, because of the brightener's greater substantivity, it also improves the brightness of the base paper. Where necessary (ie when the paper machine changes to an FBA-free grade of paper), recycled FBAs can be deliberately quenched with cationic polymers (eg imidazolines) or the FBA residues can be oxidised, both hypochlorite and ozone being effective in this respect.

Fluorescent whitening agents

This is an alternative name for fluorescent brightening agents.

Fluorine

This is the lead element in Group 17 of the Periodic Table and is present in fluoride complexes with chromium salts and in organofluorine compounds that are used for conferring grease resistance.

Fluting

Within packaging papers/boards, this is the second largest category (after linerboard). Fluting (or corrugating medium) is the inner (wavy) component of corrugated case materials and there are two distinct types - fluting made from 100% NSSC pulp and fluting made from 100% recovered paper, but many grades are made with blends of these two pulps. Fluting is made over the grammage range 105-175 g/m^2 (although it can be higher), the standard product being 127 g/m^2. It is made as a single ply product, whose key properties are stiffness, compressive strength and crush resistance.

Both types of fluting are made on paper machines with substantially and, in some cases, fully closed water systems. At NSSC pulp-based fluting mills, there is thus a strong incentive to minimise carry-over of pulping-derived dissolved solids in order to minimise build-up problems at such high levels of water closure. However, washing of such pulps is difficult so it is fortunate that manufacture of NSSC-based fluting does not need any wet end additives to achieve the required product performance. The use of chemicals to improve retention and drainage would be desirable, but the presence of dissolved lignosulphonates in the pulp makes this uneconomic.

Recycled fluting is normally made from recovered corrugated case materials, but requires the use of quite high starch addition (around 5%) to achieve the required strength. Traditionally, this starch is added by surface application (most commonly at the size press), but there is a lot of interest in replacing this with wet end addition in view of the potential for increased production when the machine operates without a size press. This change is complicated by the very high wet end concentrations of dissolved organics on such machines due to the combination of high inputs of from the recovered paper (around 50 kg/tonne as COD) and the very closed water systems.

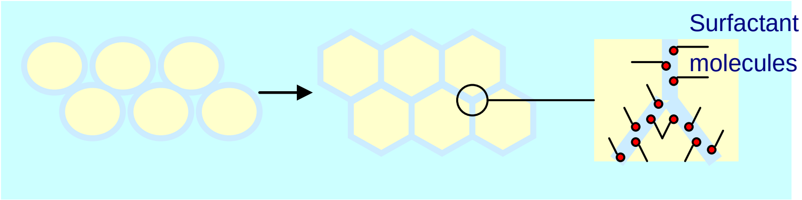
Levels of dissolved organics on such machines can easily exceed 10 g/l with concentrations of 30-40 g/l (as COD) being present on machines with fully-closed water systems and no internal wastewater treatment plant. There can also be equally high concentrations of dissolved electrolytes, which mainly originate from inadequate microbiological control leading to acid-induced dissolution of calcium carbonate. Levels of these parameters at four recycled fluting/liner mills is shown in the table below. Although not quantified in this table, a significant proportion of the dissolved organics (COD or DOC) may have been converted to organic acids (such as acetic) by microbiological activity. At one mill with a fully-closed water system, the concentration of organic acids was 12,000 mg/l (compared to a COD of 34,000 mg/l) before installation of an integrated bio-treatment plant, which reduced the circuit concentrations by 75% for both the acids and total dissolved organics.

Parameter	Mill A	Mill B	Mill C	Mill D
pH	6.6	6.4	6.8	7.8
Temperature (°C)	51	38	42	55
Conductivity (mS/cm)	9.5	6.5	5.2	16.8
Chloride (mg/l)	700	170	630	260
Sulphate (mg/l)	1800	1500	-	830
Calcium (mg/l)	2100	2000	1100	460
Hardness (mg/l $CaCO_3$)	5300	5250	2800	1200
Alkalinity (mg/l $CaCO_3$)	2900	3300	1800	6000
Langelier Index (-)	+2.0	+1.6	+1.6	+3.0
COD (mg/l)	40,000	-	-	-
DOC (mg/l)	-	10,300	3100	6700
Cationic demand (meq/l)	-	1.7	0.7	5.5
Effluent flow (m^3/tonne)	0	0.3	0	0

Source: Berard, P in Pulp Paper International, 2000, 42, 4, 44-51.

Foam

Foam is a type of stable colloidal dispersion, in this case of a gas surrounded by a thin liquid film. In addition to the gas and the liquid, a third component is needed to stabilise the foam - this is a surface active material (surfactant) such as a detergent or certain types of particulate solid. The gas-liquid interface is stabilised by the orientation of the surfactant with its hydrophobic part within the gas phase and its hydrophilic part within the water. The interfacial (surface) tension is minimised by the formation of spherical bubbles, but polyhedral bubbles are formed at higher gas contents (see representation below).



Foam stability depends on a number of factors, but the most important is the elasticity of the liquid film, ie its ability to adjust local surface tensions in response to stresses placed on it. The presence of particles within foam (having the appearance of more of a scum than a foam) has a strong stabilising effect due to their high surface viscosity. There are several sources/types of both entrained gases and surfactants in most papermaking systems so the need for some form of foam control is common, not only at the wet end, but also in surface application at the size press and in coating. The retention of wet end surfactants in the paper is inevitable (depending on the degree of water closure) and, whilst this does remove them from the wet end, re-dissolution can occur at a surface applicator, particularly at the size press due to the ease of dissolution at the high prevailing temperatures.

Foam tends to be worst on machines with in closed water systems due to the increased concentration of any surfactants present (as they are part of the dissolved solids) and the raised temperature, which lowers water viscosity, surface tension and the solubility of most gases. Foam (as opposed to the entrained gases that are the foam pre-cursors) is mainly a problem within the paper machine's backwater system, partly due to the much lower level of particulate solids (which tend to collapse foams occurring elsewhere) and due to the presence of air introduced during drainage on the formation wire. Foam sitting on the top of a tank is not in itself much of a problem (apart from unsightliness) and does mean that at least some of the surfactant load in the system is not being re-circulated with the whitewater.

Nevertheless, foam accumulation is not desirable and is indicative of the presence of free surfactants that could be causing problems elsewhere. Foam can be controlled using the same hierarchy of techniques summarised generally for all problematic substances. In terms of foam, these are:

- ❑ selecting raw materials with the lowest possible content of surface active components

  As substances with surfactant properties are widespread in papermaking raw materials, this is not easy, but significant reductions can be made by ensuring that pulps are well washed and by the use of low-foaming detergents in cleaning chemicals.

- ❑ so far as it is practicable, optimising machine operation (without chemical addition) to minimise foaming action

  Wet end foaming can be associated with the use of certain functional chemicals such as rosin and PAE wet strength agents. As this is often caused by their poor single pass retention leading to high doses, close attention should be paid to chemical efficiencies. System design is clearly important in relation to minimising the opportunities for the ingress of air and the judicious use of metallic anti-foams (spanners) to prevent ingress of air is simple and cost-effective. Mechanical degassing by the application of vacuum is used on some machines ahead of the flowbox to remove gases in the thin stock, but backwater foam can still occur due to re-aeration during stock drainage. The generation of carbon dioxide within the system through microbial activity and dissolution of calcium carbonate must be minimised, particularly as this tends to occur within backwater systems where foam can most easily accumulate.

- ❑ dosing of specific control chemicals.

  As none of these techniques can be relied on to prevent foam occurrence with approaching 100% success, the use of foam control chemicals is common. Commercial formulations of these chemicals are complex and usually contain ingredients with the following functions:

  - anti-foams to prevent the initial foam formation
  - defoamers to destroy an already-formed foam
  - degassing action to facilitate disengagement of entrained gases.

Folding boxboard

This grade is a multi-ply packaging product in which chemical pulp forms the basis for the two outer plys (liner and backs) and mechanical pulp is used largely for the middle plys. As the main use is for the packaging of food, the liner (and sometimes the backs) is usually coated. The chemistry of the liner ply using bleached chemical is similar to that of wood-free fine papers, but the back ply can use unbleached chemical pulp (such as unbleached sulphite in view of its high brightness when unbleached). The very wide range in the chemistry of the three furnishes on these machines is illustrated below in the data from a machine using bleached Kraft for the liner, RMP and broke for the middles and unbleached sulphite for the backs.

RETENTION AND CHEMICAL DATA FOR MULTI-PLY BOARD

Ply	Temperature (^{o}C)	Thick stock fines (%)	Total SPR (%)	Fines SPR (%)	Conductivity (µS/cm)	COD (mg/l)	Zeta potential (mV)
Liner	22	18	83	48	450	150	+5
Middles	39	29	91	71	490	1330	-10
Backs	19	12	15	8	280	360	-17

The retention aid on the liner ply was cationic starch, but the addition rate was constrained by sheet formation as this side of the board would be later coated. Despite the high fines content of the mechanical pulp, the absence of any formation constraints on the 60-70 g/m^2 middles plies allowed the single pass retention (SPR) to be maximised by controlled addition of polyethyleneimine (0.3-0.6 kg/tonne). The retention of the backs ply was poor due to its low grammage (20 g/m^2) and the absence of retention aid for formation reasons.

All plys were sized with alum/rosin at about pH 5.3. The conductivity originated from fresh water (170 µS/cm) and from the alum-derived sulphate (200 mg/l compared to 40 mg/l in the fresh water). The dissolved organics were high in the middles stock due to the high content of the mechanical pulp and the recycling of all broke (which contained size press starch and coating chemicals) to the middles. Despite the addition of the strongly cationic PEI polymer to the middles, the surface charge of the stock remained negative. The positive zeta potential of the liner ply was a result of both alum addition, which gives cationic species at the prevailing pH of 5.3 and cationic starch addition. The backs ply was anionic due to the lower alum dose and the high negative cationic demand of the unbleached sulphite stock (ca 100 µeq/l).

Folding endurance

This strength parameter is measured by holding the paper under tension whilst it is repeatedly folded backwards and forwards. The value is the number of folds before the paper breaks. It is mainly measured on security (cheque and banknote) papers.

Force

This manifests itself as something able to generate motion in a body and is measured in Newtons. There are four fundamental types of force in nature:

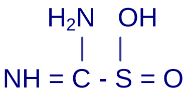
- ❑ the strong nuclear force is a very strong, but very short-ranged (active over ranges of about 10^{-15} m) attractive force that is responsible for holding the nuclei of atoms together, ie stopping the nucleus flying apart through the mutual repulsion between protons. The size of this force is demonstrated through the energy released in fusion between light nuclei and in the fission of heavy nuclei.
- ❑ the weak nuclear force is, as its name suggests, very weak with a very short range. It is responsible for radioactive decay and neutrino interactions. It governs the process called beta decay whereby a neutron breaks up spontaneously into a proton, an electron and an anti-neutrino. When this takes place within the nucleus, a new element is generated due to the change in the number of nuclear protons.
- ❑ the electromagnetic force is much weaker than the strong nuclear force, but is long-ranged. It can be attractive or repulsive and is responsible for the interactions between charged substances and

between charges substances and magnetic fields. The electromagnetic force holds electrons within atoms through their attraction to the nuclear protons and governs the emission and absorption of electromagnetic radiation such as light. Electrostatic forces between particles and dissolved substances are important in papermaking in relation to adsorption and particle aggregation.

- the gravitational force is weak, but has a very long range. It is always attractive and acts between all pieces of matter in the Universe. It is responsible for holding materials on Earth and for the orbits of moons and planets.

In addition to the electrostatic forces mentioned above, there are other important intra-molecular, inter-molecular and inter-particle forces in papermaking and these are summarised under attractive and repulsive forces.

Formadine-sulphinic acid (FAS)



$$\begin{array}{ccc} & H_2N & OH \\ & | & | \\ NH = & C & - S = O \end{array}$$

This chemical (also known as aminoiminomethane-sulphinic acid, formula at right) is generated when thioureadioxide (TDO) dissolves in water. It is a light yellow powder, which dissolves in water up to about 27 g/l at 20°C to give a slightly acidic solution (pH 4 at 10 g/l). It is much more soluble (100 g/l) under alkaline conditions as the sulphinate anion, but, as this is unstable, it is prepared as required as an alkaline solution (2:1 FAS:NaOH ratio). It yields urea and sodium sulphite/sulphate on oxidation:

$$H_2NC(NH)SO_2^- + 3H_2O \rightarrow CO(NH_2)_2 + HSO_4^- + 4H^+ + 4e^-$$

FAS is used for the reductive bleaching/colour stripping of deinked pulps and machine broke. It is usually used with stabilisers such as sodium silicate or chelating agents to stop its metal-catalysed decomposition and consequent loss of bleaching power.

Formaldehyde

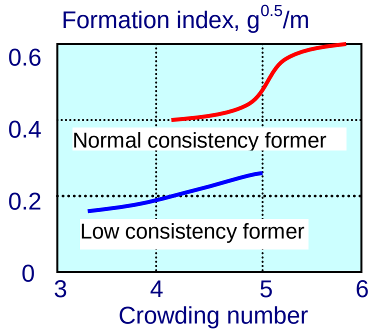
This simple aldehyde (HCHO) is not used in its own right in papermaking, but it is present in the urea-formaldehyde (UF) and melamine-formaldehyde (MF) resins used to confer wet strength on certain papers. These products have been under some regulatory pressure due to the adverse effects of formaldehyde on human health at low atmospheric concentrations. On the basis of animal tests, it is a suspected human carcinogen and most countries have thus set occupational exposure limits, eg 8-hour time-weighted averages of 0.75 ppm (USA) and 2 ppm (UK). It has also been used as an insolubiliser in paper coatings.

Formation

This term has an obvious meaning as the process whereby the suspension of pulp and other additives is formed into a paper web, but it also refers to a particular quality of the final paper, which is its micro-uniformity, ie its uniformity measured on a scale of a few millimetres. This is also called the look - through of the paper as a subjective assessment can be made simply by holding the paper up to a light source. Paper formation is of some importance from an aesthetic viewpoint in lighter-weight printing/writing papers and of minor importance in this sense in most heavier-weight packaging papers, but it is important in all paper products because of its contribution to their overall integrity and strength. Areas of poor formation quality in an otherwise well-formed paper act as a point of weakness and potential fracture/tear.

Fundamental work on ideal, random fibre networks has shown that the formation quality can be modelled on the basis of fibre length, fibre coarseness and mean grammage, but this model has not been fully verified experimentally. However, most papers do not consist only of intact fibres (but also of fines) and are produced on paper machines with many operational variables. The formation quality of the paper is influenced in a complex way by all of these factors, which can be broken down into two main categories:

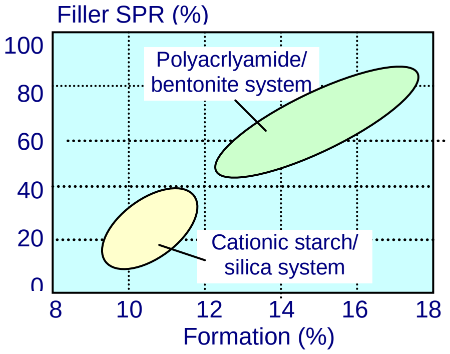
- characteristics of the furnish such as:
  - the balance of fibres and fines in the papermaking stock as the fines will fill in the gaps between the overlapping fibres, thus evening out the uniformity in all directions
  - the dimensions of the genuine fibres in the pulp as this influences their coarseness and hence their crowding number and flocculation tendency
  - the content of entrained gases in the papermaking stock, as an entrapped gas bubble within the consolidating sheet becomes a light spot (or at the extreme, a hole) once the bubble disappears
  - the presence of any additive (but notably retention and drainage aids) that affects the overall state of particle aggregation through colloidal forces
  - the addition of formation aids to limit fibre flocculation.
- characteristics of the machine system such as:
  - the design of the machine approach flow system in terms of stock hydrodynamics
  - the consistency at which the paper is formed as this influences the crowding number of the stock and its flocculation tendency (see example at right, where a low formation index denotes good formation quality)
  - the type of former, which has profound effects on many aspects of paper quality, but gap formers are generally considered to produce the best-formed paper
  - the efflux ratio at the flowbox slice
  - the angle of impingement and precise location of the stock as it contacts the forming fabric
  - the type and set-up of drainage elements on the forming fabric.



Source: Nazhad et al J Pulp Paper Science, 2003, 56, 1, 61-65.

The most important papermaking variable to control formation quality at the required level is the papermaking consistency, as shown in the above example. The optimal range of papermaking consistencies for different paper grades is well-established and this is often dictated by formation considerations. The most extreme case is tea-bag paper, which is made from long non-wood fibres such as hemp at formation consistencies of around 0.02% or 200 mg/l at the flowbox. Other grades are made in the range of 0.1-1% (1-10 g/l) flowbox consistency, but always at the highest possible level in order to minimise the size of pumps, pipes, tanks and the initial dewatering zone. The dimensioning of the papermaking system (eg fan pump capacity) is of obvious importance in relation to the ability to lower the formation consistency in order to improve the formation quality of the paper. The adverse consequence of lowering the formation consistency is a drop in single pass retention, but this can be mitigated by optimisation of the retention aid system.

There are other important interactions between formation, single pass retention and drainage. Improvements in both drainage and single pass retention (SPR) provide opportunities to enhance formation, in the case of drainage by allowing greater dilution at the flowbox without exceeding the water removal capacity of the former and, in the case of SPR, by lowering the flowbox consistency through the better quality of the returned whitewater. However, potential improvements in drainage and SPR through the addition of retention/drainage aids are sometimes constrained by their impact on fibre flocculation and hence on formation (see these diagrams for examples).



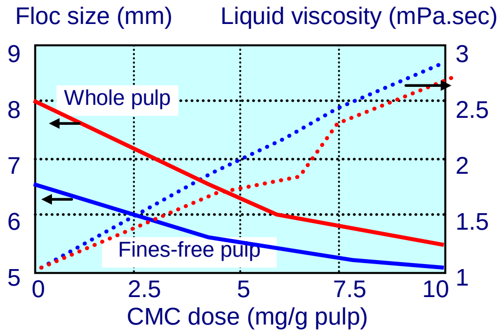
Source: Albinsson, CJ et al Tappi J., 1995, 78, 4, 121-128.

A specific example of the interaction between single pass retention and formation is shown at right for a system comprising 80% of a refined bleached softwood Kraft pulp (5% fines content) and 20% calcium carbonate filler. The work was done on a pilot paper machine running at 800 m/minute with a formation consistency of about 5.5 g/l. It is evident that the polyacrylamide/bentonite system gives the better filler aggregation and hence retention, but poorer formation (high values). Data points where both systems gave the same filler SPR (not shown on graph) indicated that the cationic starch-based system gave slightly better formation. There was no correlation between paper strength and formation when comparing the two retention chemistries as the starch-based system always gave the higher strength (due to the starch). However, the polyacrylamide-based system produced a much weaker paper (60 g/m^2) when the formation was poor and the filler retention high.

As exemplified in the two figures shown above, a number of different formation indices have been developed by researchers and also by manufacturers of commercial formation analysers. Attempts have also been made to develop a so-called universal formation index, but this has not yet been fully accepted. Most of the formation indices are based on the same principle of analysing the variance of the transmitted light from a sensor using a light or β-ray source. For example, the formation index in the first example is the standard deviation of the variation of the transmitted radiation (in that case, from a β-ray source) expressed as a grammage divided by the square root of the mean grammage. This measurement principle is similar to that used for the measurement of the state of flocculation of the papermaking stock prior to paper formation. Today, many paper machines are equipped with on-line formation sensors, although they are not used for feedback control.

Formation aids

These chemical additives are not widely used in papermaking, but may be added to the wet end stock in order to improve the formation quality of the paper, notably when working with particularly long-fibred stocks, eg softwood and some non-wood pulps. The types of chemical used are the natural gums such as guar, carboxymethylcellulose and anionic polyacrylamides. The mechanism of the action of anionic polymers appears to be a combination of steric interference preventing inter-fibre contact and a degree of charge repulsion plus viscosity-related effects.



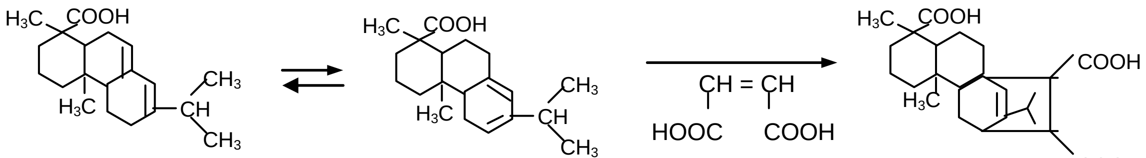
Source: Beghello in J Pulp Paper Science, 1998, 13, 4, 274-279.

An example of this effect in terms of the degree of fibre flocculation is shown in the figure at right for the addition of a low molecular mass (12k Daltons) carboxymethylcellulose (CMC) to a bleached softwood Kraft pulp refined to 25°SR. In this particular case, it seems clear that the mechanism of CMC's action is to increase the viscosity of the suspension's liquid phase (ie without the fibres present) which exerts a high viscous shear on the fibres thus lowering their relative motion and the frequency of inter-fibre contacts (but note that the negative consequence of higher viscosity is slower drainage). However, changes in water temperature (and hence in viscosity) had little effect on floc size (albeit only over the viscosity range 0.5-1.2 mPa.sec), which suggests that chemical (ie dispersing) effects do play some part in the action of CMC. Some effects of water chemistry on floc size for this same pulp are shown here.

Fortified rosin

Most rosin products contain a proportion of rosin that has been fortified to strengthen its sizing ability. This is achieved by carrying out a Diels-Alder reaction with maleic anhydride or fumaric acid, which introduces two additional carboxyl groups into levo-pimaric acid across the 1,4-diene in its third ring. The amount of levopimaric acid in rosin is small, but its reaction with the added anhydride pushes its equilibrium with abietic acid to the right (as shown below) and effectively all the abietic acid can be converted to the fortified form. In practice, the addition rate of maleic anhydride is about 25% on a molar basis and this leads to a number of benefits for the fortified product:

- reduced tendency to crystallise from solution
- lower softening temperature and consequent easier emulsifiability
- despite the molecule itself being much less hydrophobic than natural rosin, the sizing efficiency is improved and this is attributed to a combination of more optimal orientation of the rosin molecule in the paper and ease of spreading during drying of the paper.



FPR

This is an abbreviation for first pass retention.

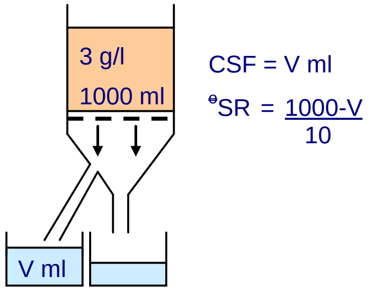
Free energy

Within thermodynamics, there are two terms for free energy:

- the Gibbs free energy (G) where G = H - TS and H = enthalpy, T = temperature and S = entropy. The most common form of this relationship is $\Delta G = \Delta H - T\Delta S$ for constant temperature conditions. A spontaneous change has to be accompanied by a decrease in free energy, ie ΔG is negative and $\Delta H < T\Delta S$.
- the Helmholtz free energy (A) where A = E -TS and E = internal energy, T = temperature and S = entropy.

Freeness

This term applies to the ease of drainage of water from the papermaking stock. It is measured in a standard apparatus by allowing one litre of the dilute pulp suspension (3 g/l consistency) to drain on a wire into a chamber with two outlets (see diagram at right). The bottom outlet is partially blocked so that the egress of water through it is restricted, but the higher side outlet has an unrestricted overflow. Pulps with fast drainage deliver most of their water quickly so that a relatively large proportion of this water leaves via the higher side outlet. The converse is true for pulps with slow drainage. It is important to standardise the water used in pulp dilution due to the known effect of electrolytes on the drainage process, the drainage rate being considerably lower for deionised/distilled water compared to tap water of various qualities. However, the drainage rate has been shown to be reasonably stable above a conductivity of about 0.2 mS/cm.



The receptacle receiving the side overflow is calibrated in two different ways:

- in units of Canadian Standard Freeness (CSF), which is the volume (ml) overflowing via the side outlet such that fast draining pulps have high values (CSF > 500 ml)
- in units of °Schopper-Riegler (°SR) such that fast draining pulps have low values (°SR < 20). The SR value is calculated by deducting the flow from the side outlet (ml) from 1000 and dividing the result by 10. This value is the percentage of water overflowing via the side outlet and, strictly speaking, is more an index of wetness as the value increases with declining drainage.

Freeness is used as an index of the progress of pulp refining and can be measured on-line using systems from companies such as BTG, Innomatic and Metso.

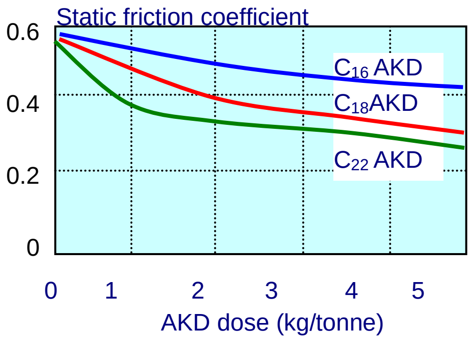
Friction

This is one of the surface properties of paper and features prominently in the study of tribology, the science of interacting surfaces in motion. Friction is defined as the resistance encountered when one body moves relative to another with which it is in contact. The coefficient of friction is the ratio of this frictional force resisting motion to the force at right angles to the surface and has two forms - the static coefficient (at the point when the body is starting to move) and the kinetic coefficient (when the body is moving). The kinetic coefficient is always less than the static coefficient with values for paper products covering the wide range 0.2-0.9. A low friction coefficient is often referred to as slip.

Generally, the friction force has an adhesive component related only to the interfacial characteristics and a deformation component related to the bulk properties (eg sheet integrity for papers) of the materials in contact. The friction of a finished paper surface is important during winding, sheet feeding, converting and stacking operations. The desirable level of friction depends on the application, two examples being:

- low-medium level of friction for copier papers to give good stackability and good sheet feeding without sticking.
- medium level of friction for the outer surface of packaging boxes so they can be stacked safely.

There is no clear consensus as to the relative importance of the adhesive and deformation terms for paper products and it seems likely that this depends on the nature of the paper concerned and how it is used. Inter-paper friction does vary with the direction of movement in terms of the orientation of the two papers to one another (MD-CD), which is related to bulk effects and surface smoothness. The latter becomes an important factor when mineral fillers are incorporated in paper as one of their benefits can be a smoother paper surface, but there are significant differences between different fillers. Regular-shaped fillers such as calcium carbonates increase friction and this has been attributed not to their shape, but to their ability to absorb surface chemicals (eg fatty acids that otherwise act as lubricants) as the increase in friction correlates well with the filler's oil absorption. By contrast, clay fillers, despite their significant oil absorption, decrease the friction coefficient and this has been attributed to the alignment of their platy surface in the x-y plane of the paper.



Source: Hoyland, Paper Technology, 2001, 42, 3, 45-49.

Not surprisingly, the presence of extractives and sizing agents, due to their surface activity, has a significant effect on friction. Papers with a high extractives content (wood-containing grades) have a low friction coefficient (ca 0.3), but, when the extractives are removed by solvent extraction, the friction coefficient can double in value. The impact of rosin and ASA sizes on paper friction is quite weak, but AKD size is well-known for its strong tendency to create a slippy paper surface. A typical effect for an unfilled wood-free paper with AKDs with 3 different alkyl groups is shown at right. It is evident that the surface friction decreases with dose and is greatest for an AKD with the longest alkyl chain. This work also showed a good correlation between friction and surface energy of the paper, the latter dropping from about 70 mN/m (0.6 friction coefficient) for the AKD-free paper to 20-30 mN/m (0.3 friction coefficient) for the heaviest-sized papers. The presence of excess fatty acid in the AKD size lowered the friction coefficient (and increased the sizing) noticeably for the C_{14}-AKD sized paper at low AKD doses, but the effect declined at higher AKD doses and with longer alkyl chain AKDs. Hydrolysis of AKD to the ketone is also known to lower the surface friction of AKD-sized papers as removal of such hydrolysis products (by solvent extraction) increases the friction coefficient (from about 0.3 to 0.4 in one quoted case).

Where necessary, the frictional characteristics of paper are controlled by chemical additions to the size press, the most common additive being amorphous silica for raising friction and various lubricants for lowering friction. Other size press additives, such as surface sizes, also influence the paper's friction characteristics.

Fresh water

The water used on the paper machine is a mixture of fresh water and water recycled after some previous use. Fresh water use affects the chemistry of the paper machine in two distinct ways:

- the quality of the water entering the paper machine circuit defines the baseline chemistry of the system, which remains constant irrespective of the degree of water closure
- the quantity of fresh water entering the paper machine circuit (ie the degree of water closure), together with the single pass retention, affects the concentration build-up of individual materials.

The quality of natural waters varies enormously from rainwater, which contains just small amounts of dissolved gases such as CO_2 and SO_2, to marine waters containing 3.2-3.6% mineral salts, largely sodium chloride. The quality of the waters used by paper mills is closer to that of rainfall, but the quality of surface or sub-surface (ground) waters is modified by materials picked up during their passage overground and/or through the soil/earth to the mill abstraction point. Paper mills use both sources of fresh water and some are in the fortunate position of having both sources available.

The treatment given to fresh water prior to use in the mill depends on the raw water quality judged against the quality of the water required for its applications in the mill, but this can include chemical coagulation, clarification by sedimentation/filtration and disinfection. The level of water treatment carried out thus changes the natural quality in terms of the particulate fraction and the microbial content, but has little effect on the dissolved solids.

The concentration and nature of dissolved solids in fresh waters is determined largely by the geochemical characteristics of the earth over or through which the water passes, but also by man-made inputs. The latter are likely to be more significant in surface rather than ground waters, due to the ability of the soil strata to attenuate the levels of many materials by adsorption, ion exchange, etc.

Materials dissolve in water either due to a natural water solubility or, particularly for carbonate minerals, due to interaction with the acidic gases present in the rain water. In general, ground waters tend to have a higher, but more stable, concentration of dissolved solids than river waters due to their long retention time beneath the earth's surface. Surface waters are subject to large seasonal variations in quality, heavy rainfall usually leading to a lowering of the concentration of dissolved solids, but a rise in the concentration of particulates.

The inorganic solids dissolved in both surface and ground waters are mainly composed of calcium, magnesium and sodium cations balanced by bicarbonate, sulphate and chloride anions. The simplest way of quantifying this material collectively is by measuring the water's conductivity, which varies from below 0.1 milliSiemen (mS) per centimetre for fresh waters with low dissolved solids to a maximum of about 1 mS/cm. Such high values are associated with brackish surface waters, ground waters suffering from saline intrusion into the aquifer or ground waters with high hardness levels due to the presence of chalk or limestone strata.

The pH of water is determined by the balance of acidic materials such as humic acids from peat and CO_2 against alkaline materials such as calcium carbonate. This is discussed in more detail under the heading of Langelier's equation. The inorganic content of a range of typical waters is shown below.

Parameter (mg/l except pH)	Ground water	Ground water	River water	River water
pH	7.1	7.6	8.2	6.7
Total dissolved solids	800	400	35	25
Total hardness (as $CaCO_3$)	420	270	35	25
Alkalinity (as $CaCO_3$)	260	250	15	20
Sodium	120	30	15	20
Chloride	100	20	20	20
Sulphate	180	30	15	5

Dissolved organic matter is normally present at quite low levels in fresh waters, particularly in the types of ground water used for public or industrial supply. Peat-derived acids have low pH values and also introduce substantial discoloration into the water, a feature that would be considered undesirable at most mills. The levels of man-made organics can be quite high in streams receiving domestic and industrial discharges. This source of organic matter is small compared to the on-machine levels originating from pulps and additives. Overall, the fresh water quality has a greater impact on the inorganic chemistry at the wet end rather than on its organic chemistry.

Fugitive sizing

This term is sometimes used interchangeably with the term size reversion to describe the situation where a paper that is fully sized at the mill is found to have lost some or all of its sizing some time later (see here for pictorial representation). Fugitive sizing is sometimes differentiated from size reversion by defining it as the complete loss of sizing over a defined period. Some researchers have argued that the term "fugitive" implies that the original sizing level will eventually be recovered, but as this is never the case, this terminology is best avoided. This practice is adopted in this document and these general effects are discussed further under size reversion.

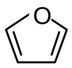
Fungi

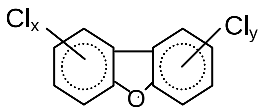
Fungi are a more complex group of micro-organisms than bacteria, but are still classified as belonging to the unicellular kingdom of the protists. They possess certain plant-like characteristics (eg a thread-like growth), but are not classified as plants for several reasons such as the fact that they have no chlorophyll. Most fungi make use of decaying or dead organic matter for their nutritional requirements and can grow in the presence of very little free water. Many fungi have the ability to break down cellulose and lignin and can thus cause problems due to their ability to grow on damp pulp and paper products. Pulp drying exercises a high degree of sterilisation for lap pulps, but semi-dry pulps can be severely contaminated with cellulolytic and disfigurative fungi such as *Aspergillus* sp., *Trichoderma* sp., *Penicillium* sp., etc. Fungi have been deliberately added to wood during storage in order to break down some of the extractives. This aids their removal during pulping and lowers the pitch content of the pulp.

Within the papermaking process, the incidence of fungal problems has declined with the move away from acid papermaking to neutral papermaking as the common aquatic fungi such as yeasts prefer an acid pH. The contamination of paper and board products with fungi is always a result of secondary infection from the local environment as, unlike some bacteria, fungi cannot resist the high temperatures during paper drying. Moulds growing on paper products are usually common air-borne organisms such as *Penicillium* sp., *Aspergillus* sp. and *Cladosporium* sp. Papers are treated with fungicide preservatives to prevent such growths.

Furans

Technically, furan is the name for the five-membered heterocyclic ring shown at near right, but this name is also used as short-hand for the chlorinated dibenzo-furans (formula at far right). These are related to the chlorinated dibenzo-para-dioxins, where their relevance to papermaking is discussed further.





Furnish

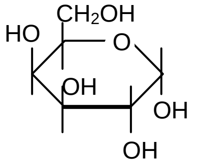
This is the traditional papermaker's term for the mixture of materials (pulps and chemicals) used to make a particular grade of paper. It is often used interchangeably with "stock", although the latter strictly only applies to the furnish as suspension prior to sheet formation.

FWA

This is an abbreviation for fluorescent whitening agent, an alternative name for fluorescent brightening agents.

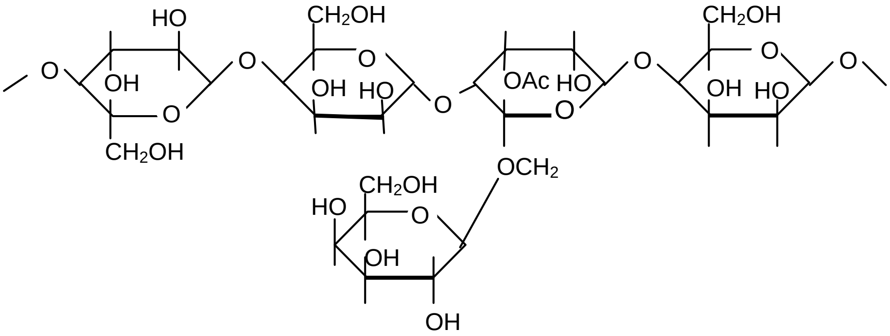
Galactose

This is one of the five monosaccharides that are present in hemi-celluoses. It is a hexose with the formula $C_6H_{12}O_6$ and the structure shown at right (drawn with a pyranose structure in the α-anomer form - see glucose for explanation of these terms). Galactose is also as one of the two monomers in guar gum.



Galactoglucomannan

This is the main hemi-celluose in softwoods, accounting for about 20% of the wood. It is a linear polymer of β-1,4-linked glucose and mannose units with single galactose units occurring as an α-1,6-linked side-chain. The acetylation of the mannose units occurs about once every 3/4 units. Its degree of polymerisation is 50-150.



There are two types of galactoglucomannan:

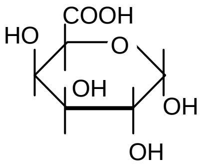
- a high galactose content polymer (as shown above) in which the relative proportions are 1:1:3
- a low galactose content polymer in which the ratio is 0.1:1:4 and this is sometimes referred to just as glucomannan.

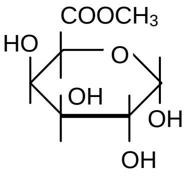
Galactomannans

These are polysaccharides that occur in certain natural gums, notably locust bean gum and guar gum.

Galacturonic acid

This is the chemical name for the monomer that comprises the major part of pectin. It has the formula $C_6H_{10}O_7$ and the structure shown at near right. Its pK_A value is about 3.7, so any pectins present in papermaking would be in the ionised form and thus contribute to the anionic trash fraction if dissolved from the pulp. Some of these units are present in wood as the methyl ester (see picture at far right), which can be hydrolysed under alkaline conditions to form the acid (eg in the peroxide bleaching of mechanical pulps) thus increasing the polymer's solubility.





Gases

Gases get into the papermaking system by two routes:

- through being taken up from the atmosphere, the main ones being:
    - oxygen, which is useful to maintain aerobic conditions
    - nitrogen, which is effectively inert under papermaking conditions
    - carbon dioxide, which is important in relation to the various carbonate equilibria and the dissolution of calcium carbonate

- ❑ by being generated in the papermaking system, the main ones being
  - carbon dioxide from microbial activity or via calcium carbonate dissolution
  - hydrogen from general anaerobic microbial activity
  - hydrogen sulphide from anaerobic microbial sulphate reduction.

In an aqueous system, gases can exist either in an entrained state or in a dissolved state, which has an equilibrium concentration determined by Henry's Law.

GCC

This is an abbreviation for ground calcium carbonate.

Gelatin

Gelatin is a polypeptide derived from the protein, collagen, which is found in bones and other connective tissue. It contains a range of amino acids with glycine and proline accounting for about half its mass. Going back some hundreds of years, it was used extensively in papermaking for sizing and strengthening the paper surface, but its use today is limited to a few speciality grades such as security papers. It has also been used to make the walls of the micro-capsules used in carbonless-copy papers.

Glassine

This is a speciality grade of paper which has a very high resistance to grease/oil and is also very impervious to air and water vapour. It is traditionally produced from a heavily-refined bleached chemical pulp so that the pulp suspension becomes a finely-dispersed gel of cellulose fines and is finally super-calendered to enhance the closed surface finish. These papers are quite transparent (like the rather similar tracing papers), but they can be made more opaque by incorporation of filler if desired.

Glass transition temperature

This is an important characteristic of polymers and is the temperature at which the polymer changes from a hard glass-like state, where the polymer chains have no freedom of motion, to a rubbery elastic state where the polymer chains can move around. It is often abbreviated T_g. In papermaking, it is particularly relevant to those polymers used as coating binders, which have T_g values of -30 to +30°C.

Glucomannans

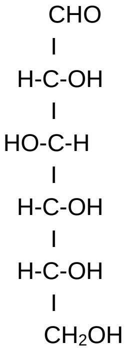
These are present as part of the hemi-cellulose fraction in hardwoods, accounting for 2-5% of the wood. It is a β-1,4-linked polymer of glucose and mannose units in a mole ratio of 1-2:1. Its degree of polymerisation is about 200.

Glucose

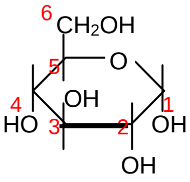
From a papermaking viewpoint, this is the most important monosaccharide as it is the sole monomer unit in both cellulose and starch polysaccharides and is also one of the five monosaccharides present in hemi-celluloses. It is a hexose with the formula $C_6H_{12}O_6$ (exactly the same as galactose and mannose), but, as with all monosaccharides, this can be written in either the open chain form ([a] below) or the pyranose ring form ([b] below). All the evidence points to the pyranose structure (a 6-membered ring with 5 carbons and 1 oxygen) being the dominant one in solution although there may be a small amount present in a furanose ring form (a 5-membered ring with 4 carbons and 1 oxygen).

The numbering of the carbon atoms is indicated on the pyranose ring form. Glucose is dextrorotatory, so, strictly speaking, should always be written as D-glucose.

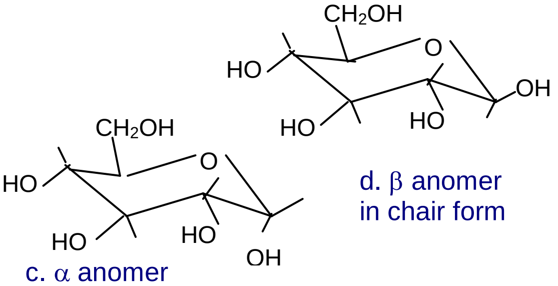
However, there is one further conformational complexity as the pyranose form of glucose has a further asymmetric carbon atom (at the carbon 1 position) and this gives rise to two further forms of D-glucose, the α and β anomers (shown as forms [c] and [d] below). Cellulose is a polysaccharide of the β-anomer and starch is a polymer of the α-anomer. In both cases, the glucose units are joined by a glucosidic linkage, but the conformation of the two chains is quite different, leading to their very different sets of properties. For some of glucose's chemical reactions (eg as a reducing agent), it is easier to visualise the reaction when glucose is shown in the open-chain form as it is the aldehyde group which is responsible for its reducing power.



a. Open chain form



b. Pyranose form for α anomer

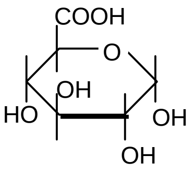


c. α anomer in chair form

d. β anomer in chair form

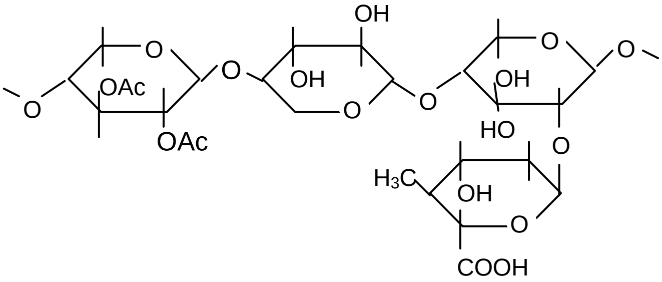
Glucuronic acid

Glucose can be oxidised to various products, but this mono-carboxylic acid is the most important in papermaking as it is responsible for the charged character of some hemi-celluoses, notably the glucuronoxylans and the arabinoglucuronoxylans. The structure of glucuronic acid itself is shown here, although it is normally present as a methyl derivative. In Kraft pulping, the glucuronic acids in the hemi-celluoses are converted to hexenuronic acids.



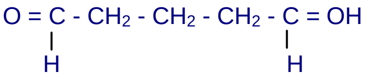
Glucuronoxylan

This is the main hemi-cellulose present in hardwoods, accounting for 15-30% of the wood depending on species. The backbone polymer is a β-1,4-linked xylan (with acetyl [Ac] substitution in the 2,3 positions of some units) with single side units of α-1,2-linked 4-O-methyl-glucuronic acids. The proportion of glucuronic acid units is only about 10% and the anionic charge on these polymers is thus typically about 0.7 meq/g. Its degree of polymerisation is about 200.



Gluteraldehyde

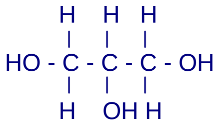
This dialdehyde is used as a biocide in papermaking and also in deinking systems, where it is particularly effective against catalase activity. Its formula is shown at right.



$$\underset{\mathrm{H}}{\mathrm{O = C}} - CH_2 - CH_2 - CH_2 - \underset{\mathrm{H}}{\mathrm{C = OH}}$$

Glycerol

This is a tri-hydric alcohol (formula at right) which is used to make rosin esters and some fatty acids in the extractives fraction of wood are present as triglyceride esters.



$$\begin{array}{ccccccc} & H & & H & & H & \\ & | & & | & & | & \\ HO - & C & - & C & - & C & - OH \\ & | & & | & & | & \\ & H & & OH & & H & \end{array}$$

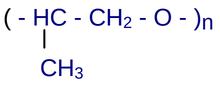
Glycols

These are defined as dihydric alcohols with the general formula shown below. The hydroxyl groups can be located on any carbon atom so their position has to be defined in the chemical name, as shown for propylene glycol. Ethylene glycol is produced from ethylene oxide, which is also used to make polyethylene glycol.

$HOH_2C - (CH_2)_n - CH_2OH$	n = 0 = ethylene glycol
$HOH_2C - CH_2 - CH_2OH$	1,3 - propylene glycol
$HOH_2C - CHOH - CH_3$	1,2 - propylene glycol

The simple glycols are not found in papermaking, but are used in the manufacture of polyurethanes. Polyethylene glycol (PEG) and polypropylene glycol (see formulae at right) are used as multi-functional coating additives, where they may act as lubricants, defoamers and plasticisers. Polyethylene glycol and polyethyleneoxide (PEO) are synonymous, the only difference being that the term PEG is used for the lower molecular mass liquid products, whilst PEO is used for the high molecular mass solids. PEGs are produced at various molecular weights from about 200 (n=4) to 9000 (n=200), which range from viscous liquids to solids (PEOs).

$- (H_2C - CH_2 - O -)_n$ polyethyleneglycol



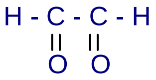
$$(- \underset{\displaystyle CH_3}{\underset{|}{HC}} - CH_2 - O -)_n$$

polypropyleneglycol

Ethylene oxide (EO) and propylene oxide (PO) can be reacted together to form EO-PO polymers which are also used as defoamers. Derivatives of short-chain PEGs (such as R - $[O\text{-}CH_2\text{-}CH_2]_8OH$ where R is a long-chain alkyl or aryl group) are used as nonionic surfactants. The term ethoxylated polymer is sometimes used to describe these latter materials. They usually take the form of either aryl-substituted derivatives such as the nonylphenol-ethoxylates (NPEs) or alkyl-substituted derivatives such as the fatty alcohol-ethoxylates. NPEs have been under some environmental pressure in recent years due to their alleged involvement in endocrine disruption in rivers.

Glyoxal

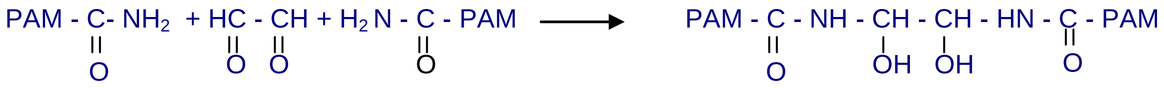
This simple dialdehyde (formula at right) can be used as an insolubiliser in coatings and is also used to make polyacrylamide-based wet strength agents.



$$H - \underset{\displaystyle O}{\underset{||}{C}} - \underset{\displaystyle O}{\underset{||}{C}} - H$$

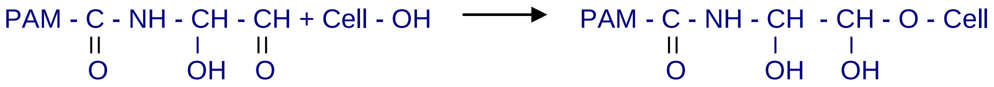
Glyoxalated polyacrylamides

These chemicals are used as wet strength agents, but impart only a temporary wet strength to the paper. They are generally made from a cationic polyacrylamide produced by co-polymerising acrylamide with a small percentage (<10% on mole basis) of a cationic monomer such as dimethyldiallylammonium chloride. This ensures that the resultant glyoxalated polymer has good adsorption on the particulate matrix. The polyacrylamide chains are cross-linked with glyoxal via some of the amide groups as follows:



$$PAM - \underset{\displaystyle O}{\underset{||}{C}} - NH_2 + H\underset{\displaystyle O}{\underset{||}{C}} - \underset{\displaystyle O}{\underset{||}{C}}H + H_2N - \underset{\displaystyle O}{\underset{||}{C}} - PAM \longrightarrow PAM - \underset{\displaystyle O}{\underset{||}{C}} - NH - \underset{\displaystyle OH}{\underset{|}{CH}} - \underset{\displaystyle OH}{\underset{|}{CH}} - HN - \underset{\displaystyle O}{\underset{||}{C}} - PAM$$

Some of the amide groups react with only one of the glyoxal aldehyde groups, thus leaving an aldehyde group available for reaction with cellulose hydroxyls to form a hemi-acetal bond as follows:



$$\text{PAM} - \underset{\underset{\text{O}}{||}}{\text{C}} - \text{NH} - \underset{\underset{\text{OH}}{|}}{\text{CH}} - \underset{\underset{\text{O}}{||}}{\text{CH}} + \text{Cell} - \text{OH} \longrightarrow \text{PAM} - \underset{\underset{\text{O}}{||}}{\text{C}} - \text{NH} - \underset{\underset{\text{OH}}{|}}{\text{CH}} - \underset{\underset{\text{OH}}{|}}{\text{CH}} - \text{O} - \text{Cell}$$

This reaction with cellulose takes place very rapidly at acid pH (4-6), but is still rapid enough at neutral pH (6-8) for the sheet to be at least 80% cured at the reel of the paper machine. Full cure can be guaranteed within 48 hours of manufacture. In use under wet conditions, the duration of the wet strength depends to some extent on the resin's chemistry with most grades losing about 25% of the wet strength after 30 minutes and 50% after several hours, but this can be shortened if necessary. The quality of the contact water is important as the hemiacetal bond with cellulose is very labile under alkaline conditions and this loss of wet strength at high pH is exploited in the normal repulping conditions for broke. This can be accomplished within 10 minutes contact time at ambient temperatures with caustic soda addition or alternatively at elevated temperatures (50°C) at neutral pH.

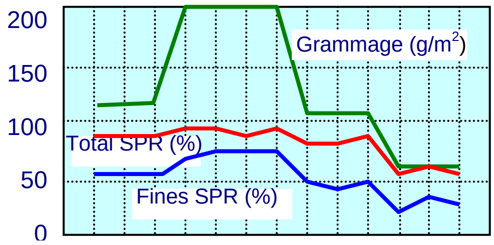
The level of wet strength achievable with these resins is high and they also give a very significant increase in dry strength, which may obviate the need for separate addition of a dry strength agent. Although the cationicity of these resins is low (<1 meq/g solids), their adsorption and retention is adversely affected by anionic trash with even sulphite ions exerting a negative on resin performance. The wet end pH should be kept below 7 with a low bicarbonate alkalinity (< 150 mg/l as $CaCO_3$) as this ionises in the drying section to release hydroxyl ions which destroys the wet strengthening action. These resins are supplied at about pH 3 in various strengths up to about 20% solids content, but the shelf-life decreases with solids content due to the more rapid polymerisation. Like all wet strength agents, these resins are best added at the end of the thick stock system at a point of good mixing.

Grammage

This is the term for the areal mass of the paper, which is sometimes referred to as its basis weight and is most commonly expressed in units of g/m^2. In North America, the grammage of boards can be expressed in pounds per 1000 $feet^2$ where 100 g/m^2 is 20.5 pounds per 1000 $feet^2$. The grammage of a paper has no direct bearing on the raw materials used to make a particular grade of paper, but, as its strength is directly proportional to its grammage, the balance of pulps used may change at different grammage levels, eg greater proportion of softwood compared to hardwood pulp as the grammage decreases.

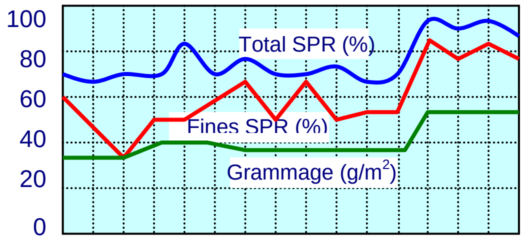
Grammage impacts on wet end chemistry through its effect on the efficiency of the filtration process in relation to the single pass retention of fines. This is illustrated in the two examples here for two different paper machines, but both making wood-free fine papers containing clay filler. The data points cover about 4 days of papermaking in both cases.

The first set of data is for a machine where the furnish is poorly flocculated and where the single pass retention (particularly of the fines) is thus critically dependent on the efficiency of solids capture by sieving/filtration. Some variability in single pass retention is an inherent feature of papermaking, but it can be moderated by the controlled use of retention aids, eg by increasing the retention aid



dose in-line with a known grade change to a lower grammage. Further data is given here for the trend in rosin retentions on this same paper machine.

The second example is from a machine where, in contrast to the previous example, the furnish is well-flocculated. Despite the low product grammage and high fines content of the thick stock (data not shown), the single pass retentions are not bad, but show significant variability due to the low grammage of the paper being made. It is noticeable that this variability in SPR, particularly of the fines, is much less at the higher grammage where the SPR is itself also higher. Further data is given here for the trend in sizing on this same paper machine.



Greaseproof papers

Ordinary papers have a degree of resistance to grease and oil because of the natural hydrophilic character of cellulose. However, this resistance can be enhanced by mechanical treatment of the paper (as in glassine papers), by acid treatment of the surface (as in vegetable parchment) or by treatment with chemicals such as organofluorine compounds or chromium/fluoride complexes.

Groundwood pulps

This is the original mechanical pulping process, which was developed initially during the mid-19th century and then further improved during the 20th century. It consists of passing debarked logs (1-1.5m long) between a large rotating grinding stone and a stationery bedplate in the presence of water, during which the individual fibres or clumps of fibres are separated. The water acts as a cooling medium, as nearly all the electrical energy is converted to heat and as a lubricating medium to lower the friction between the stone and wood, thus reducing the power input required.

The temperature of the grinding stage is an important variable as this determines the location within the fibre wall where fracture takes place and this influences the particle size distribution of the pulp, ie the balance between genuine fibres and fibre fines. The optimum temperature is close to the glass transition temperature of the lignin (about 90°C) so that the fibres are in a flexible state as the grinding action takes place, but higher temperatures produce stronger, albeit less bright, pulps. The glass transition temperatures of cellulose and hemi-celluloses is much lower (about 20°C). The temperature at the grinders is controlled by the temperature of the returned water and the quantity of shower water applied. Typical temperatures are 70-80°C for the shower water with a stock temperature of about 90°C.

The basic stone groundwood process has been developed in two ways:

- in the thermo-groundwood (TGW) process by raising the grinding temperature, but still operated at atmospheric pressure. This variant is little used.
- in the pressurised groundwood (PGW) process by carrying out the grinding under pressure (2-3 bar) and hence at higher temperature (110-120°C in stock and 70-100°C in the shower water), which allows greater control of the temperature and of the resultant pulp quality. The super PGW (PGW-S) process operates at even higher pressures (4-5 bar) and temperatures (130-140°C in stock and 95-120°C in the shower water).

The family of groundwood pulps show a progressive improvement in strength as the pressure/temperature is increased:

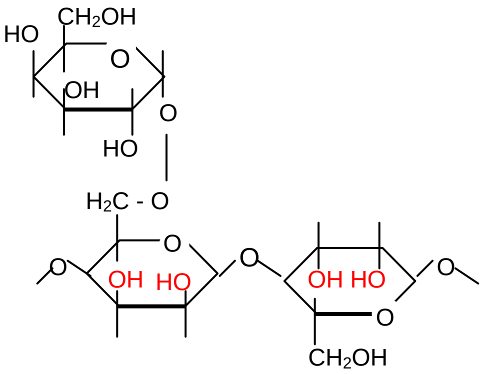
- the basic SGW pulps give a reasonable mix of strength, light scattering and brightness, but poor wet web strength (impaired runnability) with a requirement for relatively large proportions of bleached chemical pulp to compensate for their inherent weakness. They have the highest fines content, which can exceed 40% for fir and pine, but is more typically around 35% for spruce.
- the normal PGW pulps with enhanced dry strength (+20% over SGW) and wet web strength (+50% over SGW) but slightly lower brightness and light-scattering. These are good all-round mechanical pulps most suitable for SC papers and boxboard. The fines content is around 30% for spruce.
- the lower temperature PGW pulps with similar strength and light-scattering to the normal PGW pulps, but higher brightness. These pulps are best for demanding LWC grades.
- the Super PGW pulps with greater strength (+20% wet and +10% dry) than normal PGW, but slightly lower brightness and light-scattering. They have the lowest fines content (26-28% for spruce) and are best for newsprint grades.

Groundwood pulps are increasingly being bleached to increase their brightness and two examples of the effect of bleaching on the chemistry of groundwood pulps is shown here for the effect of caustic soda dose on the dissolution of organics and here for the change in dissolved organics from an SGW pulp through a peroxide bleach plant. Although furnishes with mechanical pulps are usually not sized, it is sometimes necessary (eg with newsprint) and an example is given here of AKD sizing for a groundwood pulp.

Guanidine

The formula of guanidine is $(H_2N)_2C=NH$, but it is usually used in the form of soluble salts such as the hydrochloride. Guanidine derivatives are used as biocides, eg dodecylguanidine.

Guar gum



This natural hydrocolloid gum is a galactomannan polymer obtained from the guar plant. The polymer has a backbone of β-1,4-linked mannose units with, on average, one α-1,6-linked galactose unit on every second mannose unit, as illustrated at right (unlike the galactomannans in locust bean gum). The β linkages give the polymer a straight linear conformation (like cellulose) with the pendant galactose units restricting the number of inter-molecular hydrogen bonds. Its molecular weight in the native state is 1-2M Daltons. Like starches, guar gums can be derivitised to produce esters (eg phosphates) and ethers (carboxymethylguar, hydroxypropyl-guar and cationic/amphoteric guars). Their main use in papermaking is as a dry strength additive for either wet end or surface application at addition rates up to about 5 kg/tonne. It can also be used in its natural form as a formation aid.

Despite its nonionic character, it is possible to use unmodified guar at the wet end due to the strong hydrogen bonding possible between cellulose and with galactomannans, which is attributed to the hydroxyls at positions 2 and 3 (in red above) being on the same side (cis position, unlike their trans position in galactose). It is believed to be adsorbed close to 100% at doses up to about 2.5 kg/tonne pulp. This gives enhanced paper strength due to better bonding and a more even formation, but can have a negative impact on drainage and hence on machine productivity.

Despite these possibilities with natural guar, it is most commonly used as a cationic derivative at the wet end due to the enhanced adsorption on negatively-charged particulates. As with starches, however, anionic guar derivatives may be more effective in systems containing high levels of cationic additives (eg wet strengthened papers). In this cationic form, guar gum can give improved fines retention and good drainage at the same time as good paper formation due to its relatively low molecular mass. For this reason, it has begun in recent years to be used with colloidal silica in one of the variants within Eka's Compozil system. Native or modified guar gums may also be used for size press addition due to their good film-forming ability and incorporated in pigment coating formulations due to their ability act as rheology modifiers and water retention agents.

Gum arabic

This has been used as a dispersant for the coating pigment, satin white and to make the walls of the micro-capsules used in carbonless-copy papers. It is a complex and variable mixture of arabino-galactan oligosaccharides and polysaccharides plus glycoproteins.

Gums

These hydrocolloids are usually defined as polysaccharides that swell in water to give gels or viscous solutions. Three gums have found application in papermaking - guar gum, locust bean gum and gum arabic. A chemically-related set of substances are the alginates, which are also used in papermaking.

Gypsum

This is a hydrated form of calcium sulphate ($CaSO_4.2H_2O$), which is used as both a wet end filler and a pigment in paper coating (mainly of LWC grades), but it is not, at least yet, widely used in papermaking. It is obtained as a by-product from the production of phosphoric acid and from flue gas-desulphurisation plants. Gypsum is somewhat lighter than clays and calcium carbonates, so can be used at a lower coating weight for equivalent performance. It is also brighter than the more conventional low-cost pigments.

Its potential disadvantage is its solubility when used either directly at the wet end as a filler or when coated broke is recycled. In both cases, this elevates the levels of dissolved calcium and sulphate, both of which would normally be considered undesirable at the wet end. However, in most other situations, this undesirability is due to the fluctuating levels of these ions as their sources are not being managed. However, when the main source is either wet end filler or machine broke, the concentrations should be more stable as they must approach that of a saturated solution of calcium sulphate.

This solubility means that the paper machine has to be operated with a substantially closed water system, otherwise the overall gypsum retention will be poor. These conditions should allow the use of wet end additives optimised for this rather different wet end chemistry. An example is the use of anionic starch, which has been shown to be an effective alternative to the more normal wet end cationic starch on a machine using 10% gypsum as a filler. The conductivity of this system approached 4 mS/cm and starch doses of 0.5-1% (with 1-2% PAC) gave improved body and surface strength.

Halogens

This is the name for the elements in Group 17 of the Periodic Table. All are strongly electrophilic (although this does decrease substantially down the Group), forming halide ions (X^-). Fluorine, chlorine and bromine exist as diatomic molecules (X_2) and feature in various papermaking chemicals in several different forms:

- in the case of chlorine as the element itself or as the hypohalous acid/hypohalite ion, both of which are strong oxidising agents
- in the case of chlorine and bromine as the halide ion (eg chloride) in inorganic chemicals (eg sodium chloride and sodium bromide) and as the counter-ion with many cationic polymers
- in the case of all three halogens as organohalogen compounds.

Hardness

This term can be used in two different contexts in papermaking:

- in terms of water hardness.

  The total hardness is the sum of all the calcium and magnesium salts in the water, but there are three other hardness sub-fractions:

  - the calcium component of the total hardness, eg calcium bicarbonate and sulphate
  - the temporary hardness, which is same as the bicarbonate hardness, ie the fraction removed on boiling the water
  - the permanent hardness, which is all the forms not present as bicarbonate hardness, mainly as sulphates or chlorides.

  As with all soluble substances, the hardness concentration on the paper machine depends on its input load and the degree of water closure (see these values for several machines with fully-closed water systems). Irrespective of its form, it is usually expressed in terms of calcium carbonate, eg mg/l $CaCO_3$, but it is sometimes expressed in degrees (^{o}dH) where 100 mg/l $CaCO_3$ = 10 French ^{o} = 14.3 English ^{o} = 17.8 German ^{o}.

- in relation to the hardness/softness properties of minerals.

  This is applied mainly to fillers and pigments and is measured on the Mohs scale, which ranges from a value of 1 for the softest material (talc) to 10 for the hardest (diamond). This property is important in relation to the mineral's abrasion characteristics.

Hardwood

This is wood from deciduous trees, which is widely used for conversion into papermaking pulps. The name reflects the fact that the wood in these trees is somewhat denser than in softwoods, typically around 500 kg dry substance per m^3 of total wood or around 1000 kg dry substance per m^3 of the fibre wall. Hardwoods are valued for their ability to form papers with excellent formation combined with reasonable strength and opacity.

Hardwoods are of more recent origin than softwoods and show greater complexity and specialisation in their cell structures. Genuine fibres make up the bulk of most hardwoods, the fibre length being generally 1-1.5 mm depending on species with a fibre diameter of 20-25 microns (see table below for other physical characteristics). Hardwoods also contain about 10% of bulky vessel elements and parenchyma ray cells. The cellulose content of hardwoods is similar to that of softwoods (43-45%). However, hardwoods have a lower lignin content than softwoods (typically 20-25% compared to 26-32%) and higher hemi-cellulose content (typically 30-35% compared to 25-30%). The hemi-celluloses in hardwoods are predominantly glucuronoxylans. The extractives content of hardwoods is lower than softwoods.

The main types of hardwood grown for papermaking are birch and eucalypts with other species (eg aspen and acacia) also being used depending on the growing region. Hardwoods are not generally used to make mechanical pulps or unbleached chemical pulps (due to their short fibre length) and are thus mainly used to make bleached chemical (Kraft) pulps. They are predominantly used in the various grades of wood-free fine paper as a complimentary pulp to the stronger softwoods. The hardwoods provide better light-scattering/opacity and more even formation.

Hardwood	Fibre length (mm)	Fibre diameter (µm)	Fibre wall thickness (µm)	Coarseness (mg/m)
Birch	1.8	20-25	3-4	0.1
Eucalypt	0.7-0.9	12-18	3-5	0.07-0.1

Hectorite

This is a type of smectite clay with similarities to bentonite and talc. It is best described as a magnesium silicate that also contains sodium and lithium ions. It has been used for many years in an acid form as a pigment in the back coating layer of carbonless-copy papers and has recently begun to be used as a micro-particle retention aid with polyacrylamides. Synthetic hectorites are also used as a paper coating where conductive or anti-static properties are required.

Hemi-celluloses

As distinct from α-cellulose, these carbohydrates are sometimes referred to as β- and γ-celluloses, both being soluble in 17.5% NaOH solution, but the β-celluloses are precipitated on acidification. There are probably some covalent bonds between lignin and the hemi-cellulose fraction, but the association with cellulose is solely via hydrogen bonds. Their chemical composition is very heterogeneous as, unlike cellulose, they are based on combinations of five monosaccharide units or derivatives thereof - glucose (as in cellulose), arabinose, galactose, mannose and xylose. The polymer chains are much shorter than cellulose, containing no more than about 200 units (molecular weight < about 30,000 Daltons), but some are branched. The hemi-celluloses are more uniformly distributed across the fibre wall than are cellulose and lignin, but their concentration is greatest (about 40%) in the secondary layer. Hemi-celluloses are higher in hardwoods (30-35%) than softwoods (25-30%).

Hemi-celluloses are of particular importance to wet end chemistry due to their potential dissolution (notably under alkaline conditions after the lignin has been removed) and as the more common hemi-celluloses contain anionic groups. This negative charge originates from carboxyl groups in the form of uronic acid derivatives of the sugar unit, eg glucuronic acid, which have pK values in the range pH 3-5. The main hemi-celluloses are:

- ☐ arabinoglucuronoxylans accounting for 5-10% of softwoods
- ☐ uncharged galactoglucomannans accounting for about 20% of softwoods
- ☐ glucuronoxylans accounting for 15-30% of hardwoods
- ☐ uncharged glucomannans accounting for 2-5% of hardwoods

The total carboxyl content covers a wide range (150-350 meq/g) depending on wood species, but not all of this charge is accessible for chemical interactions. One other substance that is chemically similar to some hemi-cellulose units is pectin.

Henry's Law

This is the law that determines the dissolution of gases, but is only strictly applicable when the gas is not too soluble in water:

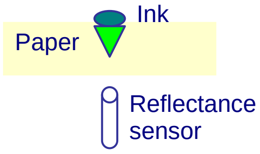
$$c = K_H.p = K_H.x.P$$

where c = gas concentration in water,
K_H = Henry's Law constant, which varies with temperature
p = partial pressure in gas phase, x = mole fraction in gas phase and P = total pressure

Gas solubility is discussed for carbon dioxide, oxygen and hydrogen sulphide and is also relevant to discussion of entrained gases and foam. It should be noted that it is quite common to observe dissolved gas concentrations well above the equilibrium value due to local super-saturation effects. This is because the kinetics of gas exchange between the liquid and gas phases is relatively slow.

Hercules size test

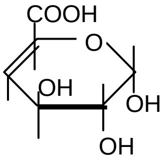
This is one of the laboratory techniques for measuring the degree of paper sizing against water and is often abbreviated HST. This method involves measuring the time for a water-based dye (Naphthol Green) to traverse the paper's z-direction, the time when the ink reaches the other side being measured by the change in surface reflectance (see diagram at right). The aqueous dye solution contains formic acid to give reasonable test times and seems to be suitable for testing calcium carbonate-filled papers, despite its possible reaction with this component of the paper.



Unlike the Cobb value, the value gets larger as sizing develops so can provide a more sensitive index of the degree of hard sizing. A waterleaf (unsized) paper will have a very low HST (few seconds) whereas sizing can increase the HST to 100s of seconds. There are several examples in this document of sizing effects using the HST technique - here for the effect of PCC content, here for a comparison of AKD and alkenyl KD sizing plus several for ASA size.

Hexenuronic acids

These compounds are formed during Kraft pulping by an elimination reaction of the O-methyl-glucuronic acid units on the glucuronoxylans and the arabinoglucuronoxylans. The formula of the monomer unit is shown at right.



Hexose

These are monosaccharides having 6 carbon atoms, three being important in papermaking - glucose, galactose and mannose. All three occur in hemi-celluloses and glucose is also the sole monomer unit within cellulose and starch.

HLB

This is an abbreviation for hydrophile-lipophile balance.

Hornification

This term is applied to the loss of swellability and flexibility of fibres when they are dried and is one of the main reasons why chemical pulps lose some of their strength on repeated recycling. The loss of swelling is usually attributed to collapse of the lumen and the formation of irreversible hydrogen bonds across its sides.

HST

This is an abbreviation for the Hercules size test.

Humectants

These substances help to retain moisture in paper products and, where required, are usually added by surface application. Chemicals function as humectants if they have a high hydrogen-bonding ability, two examples being the polyhydric alcohols, glycerol and sorbitol.

Humic acids

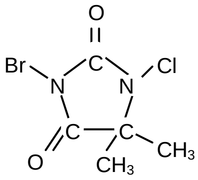
These substances are present in natural waters as a result of leaching from soils. They are chemically not dissimilar to lignin compounds, being complex aromatic macromolecules with amino acids, amino sugars, peptides and aliphatic compounds involved in linkages between the aromatic groups. Humic acids is the fraction of humous substances that is not soluble in water under acidic conditions (pH < 2), but is soluble at higher pH values. There is a second fraction (fulvic acids) that is soluble in water under all pH conditions. These acids give the water either a light yellow/yellow-brown colour (fulvic acids) or dark brown/black colour (humic acids). Humic acids contain 4 - 9 meq/g of acidic groups such as carboxyls attached to aromatic rings, whereas fulvic acids have higher somewhat levels (9 - 14 meq/l). Humic acids contain a higher carbon (50-60%) and lower oxygen (30-33%) content than fulvic acids (44-50% for both carbon and oxygen). Humic acids are more prevalent in waters draining forest soils, whereas fulvic acids are more common in waters draining grassland soils. If not removed from fresh waters, these substances contribute to anionic trash levels on paper machines.

Hydantoins

These compounds are used in a halogenated form as on-machine biocides and also sometimes for water disinfection. The most common is the 1-chloro-3 - bromo-5,5-dimethyl-hydantoin as shown at right. Other forms are the 1,3-dichloro-5,5-dimethyl-hydantoin and 1, 3 - dichloro-5-ethyl-5-methyl-hydantoin. They hydrolyse with water to form an equilibrium mixture as shown below:

$$\text{Hydantoin - Cl/Br} + H_2O \rightarrow \text{Hydantoin} + \text{HOCl/HOBr}$$

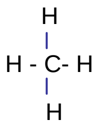
As the hypohalous acids are used up through their disinfecting action, the halogenated hydantoin ionises further to re-establish the equilibrium balance. This has the advantage over sodium hypochlorite or hypobromite that the low instantaneous concentrations minimise side reactions with organic substances and the production of halogenated (notably chlorinated) organics.



Hydrocarbons

These are the simplest type of organic compound as they contain only carbon and hydrogen. Being strongly hydrophobic chemicals, they are incompatible with water-based papermaking systems and are thus not commonly used although some defoamers are based on hydrocarbons.

Hydrocarbons can be traditionally classified into open chain (acyclic) compounds such as hexane (see below) and closed chain, cyclic compounds such as cyclohexane (see below). A special class of cyclic hydrocarbons are the so-called aromatic hydrocarbons based on the benzene ring (see below).



$$\begin{array}{c} H \\ | \\ H - C - H \\ | \\ H \end{array}$$

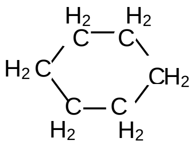
Methane

$CH_3 - CH_3$

Ethane

$CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3$

Hexane



Cyclohexane

The following terminology is useful in understanding the hydrocarbon component of some organic chemicals that are used in papermaking:

- saturated hydrocarbons

  The term "saturated" means that the carbon atoms in such hydrocarbons are always connected to adjacent atoms by single C - C bonds and each carbon atom is thus bonded to four other atoms (as shown above for hexane and cyclohexane). These hydrocarbons are called paraffins or alkanes and have the general formula C_nH_{2n+2} for the acyclic compounds, the simplest alkane being methane followed by ethane (see above) and propane (C_3H_8). The term "alkane" leads to the general name alkyl for groups such as methyl ($-CH_3$), ethyl ($-C_2H_5$), etc. These short alkyl chains are present in some papermaking materials such as the methyl esters in some hemi-celluloses. The longer alkyl groups play an important role in some fatty acids present in papermaking additives and in some sizing agents. Chlorinated paraffins are used as solvents in some carbonless-copy papers and paraffin waxes are used for their barrier effects in some packaging papers.

- unsaturated hydrocarbons:

  The term "unsaturated" means that the carbon atoms in such hydrocarbons are connected to either two or three adjacent atoms, there thus being two types of unsaturated hydrocarbon:

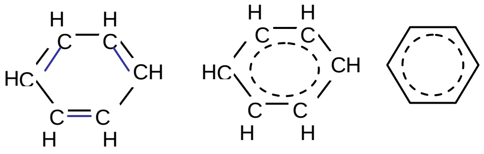
  - those with C = C double bonds, which are called alkenes or the traditional term, olefins. The term "alkene" leads to the general term "alkenyl" for groups such as ethenyl ($- C = CH_2$). The simplest alkene is ethylene (see below) and alkenyl succinic anhydride sizes are made from long-chain (higher) alkenes. Some compounds contain more than one double bond, the simplest example being dienes with two double bonds, such as butadiene (see formula below), which is used to make coating latices. A diene structure is also contained within the ring structure of levopimaric acid, which allows it to react with maleic anhydride to form fortified rosin size.

$CH_2 = CH_2$

Ethylene (ethene)

$CH_2 = CH - CH = CH_2$

Butadiene



Benzene

  - those with alternating single and double bonds (like butadiene), when the structure is said to be conjugated, meaning that some of the bonding electrons are delocalised and all the bonds are in fact equal (see valency for further discussion of this). A special case of this is the structure of the benzene ring (see formulae above), which has 3 single and 3 double bonds, but where the bonds are in fact all identical due to conjugation. The formula of benzene is thus often written as shown above at far right with a dotted circle representing the delocalised double bonds within the carbon ring. Conjugation (but involving not only carbon atoms) is very important to the colour of dye molecules.

  - those with triple C ≡ C bonds, which are called acetylenes or alkynes and have the general formula C_nH_{2n-2}. The simplest alkyne is acetylene (C_2H_2), but alkynes have no importance in papermaking.

Hydrocolloids

This general term is used to describe hydrophilic, water-soluble polymers of vegetable, animal, microbial or synthetic origin, that generally contain many hydroxyl groups and may also be polyelectrolytes. Because of their high hydroxyl content, they interact strongly with water molecules via hydrogen bonds. There are many hydrocolloids used in papermaking - starches, gums, CMC, etc.

Hydrogen

Hydrogen (H) is the first element in the Periodic Table and is a diatomic gas (H_2). Although it is not used in the papermaking process, it can occasionally be present within paper mills as it can be generated through microbiological processes operating under anaerobic conditions. There have been instances where the build-up of microbially-generated hydrogen in stagnant zones has caused explosions resulting in human fatalities at paper mills. Before the hydrogen is released to the atmosphere, it is also able to depolarise the electrochemical cell at the surface of iron pipes/tanks and thus expedite corrosion (see this figure).

Hydrogen bonds

This is a special type of bond that exists when hydrogen is covalently-bonded to small, electrophilic elements such as fluorine, oxygen and nitrogen. In such bonds, the bonding electrons are displaced towards the electrophilic element and the hydrogen acquires a small positive charge. As the hydrogen atom is very small, this charge gives the hydrogen atom a very high charge density which can attract other positively-charged entities such as the electrophilic end of other molecules. Hydrogen bonds are much weaker than covalent bonds and decrease in strength from fluorine (about 40 kJ/mole) through oxygen (about 30 kJ/mole) to nitrogen (about 10 kJ/mole). The presence of the hydrogen bond explains the anomalous properties (eg higher-than-expected boiling points) of many molecules such as hydrogen fluoride, water and acetic acid. The hydrogen bond is normally indicated by a dotted line as in H - O - H····O - H.

In papermaking, the hydrogen bond is very important to the chemistry of cellulose, there being two different sorts of bond:

- ❑ internal (intra-molecular) hydrogen bonds between specific hydroxyl groups on adjacent glucose units on the same cellulose molecule. There are two such bonds between each glucose unit and this helps to maintain the straight conformation of cellulose, which allows a close alignment between adjacent chains.
- ❑ external (inter-molecular) hydrogen bonds between specific hydroxyl groups on glucose units on adjacent cellulose molecules. Each glucose unit can form two such bonds (one on either side) to glucose units on two separate cellulose molecules. The multiplicity of these bonds explains:
    - the insolubility of cellulose, as the water molecules cannot gain access to separate and dissolve the molecule and
    - the basic dry strength of paper products, which is due to the hydrogen bonds formed between conforming cellulose fibres/fines as the paper is dried.

Hydrogen bonds can also form between the free hydroxyl groups on cellulose and other papermaking additives such as starch, aluminium polymers, dyes, gums and water molecules. The latter is particularly important to the final drying stage of water removal.

Hydrogen peroxide

This chemical (H_2O_2) can act as both an oxidising agent or a reducing agent:

Oxidising under acid conditions : $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ where E_H^o (redox potential) = +1.78 volts

Oxidising under alkaline conditions : $H_2O_2 + 2e^- \rightarrow 2OH^-$ where E_H^o (redox potential) = +0.88 volts

Reducing: $H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$ where E_H^o (redox potential) = -0.68 volts

From the relative potentials of the first and last reactions, it is evident that hydrogen peroxide should be able to oxidise/reduce itself to oxygen and water, but this reaction is very slow except in the presence of catalysts such a metal ions like manganese.

Hydrogen peroxide is a colourless, syrupy liquid that is weakly acidic, pure solutions having a pH of 4.5-5. However, commercial products are more acidic (pH 1-2) as this protects the peroxide from decomposition. Although pure hydrogen peroxide is fairly stable, it does decompose into water and oxygen when heated above about 80°C and also decomposes in the presence of numerous catalysts such as most metals, acids or oxidisable organic materials. Commercial solutions are sold as concentrated liquids with peroxide contents from 35-70% and containing stabilising chemicals (chelants) to prevent decomposition.

Hydrogen peroxide is not used in papermaking itself, but it is used as an on-machine biocide in the form of peracetic acid. However, it is widely used upstream of the paper machine for both pulping and bleaching applications:

- pulping of virgin fibres
  - in the production of a certain type of chemimechanical pulp
  - in the production of some non-wood pulps
- bleaching of virgin and recycled pulps
  - for reinforcing the extraction stage in the production of ECF pulps
  - as one of the main bleaching agents in the production of TCF pulps
  - as a bleaching or brightening agent for mechanical pulps
  - as a bleaching or brightening agent for deinked pulps.

It is always used for bleaching under alkaline conditions with added caustic soda, as this generates what is believed to be the active bleaching entity - the perhydroxyl anion (OOH^-). Stabilising agents such as sodium silicate and chelants are always used with hydrogen peroxide to prevent decomposition and maximise efficiency. In deinking systems, there is often the additional problem of catalase activity, the severity of which depends on a number of factors (peroxide dose, temperature profile), but is most reliably controlled by the addition of glutaraldehyde.

One of the major issues in the use of hydrogen peroxide for bleaching mechanical and deinked pulps is the substantially increased dissolution of organics (due to enhanced fibre swelling under the alkaline conditions) and the introduction of new charged (anionic) groups due to its oxidising action. For bleaching mechanical pulps and wood-containing recovered papers, peroxide is able to oxidise carbonyl (C = O) groups in quinoid structures to carboxylic acid groups (see reaction here) and cleave C = C bonds, thus destroying their conjugated structure and colour. Some of the chemical changes that take place during peroxide bleaching of a PGW pulp are described here and an example of the dissolution of organics in the bleaching of a groundwood pulp is shown here.

In deinking systems for wood-containing recovered papers, hydrogen peroxide is often added at the pulper stage to offset any lignin darkening from the high initial pH and then again in the final bleaching stage. Hydrogen peroxide is less effective in decolorisation or colour-stripping of dyed papers, which requires the use of reductive bleaches, either sodium hydrosulphite or FAS. A side benefit of final peroxide bleaching is a substantial reduction in the deinked pulp's bacterial content (see example here).

Hydrogen sulphide

This is one of the forms of the various sulphide species that can occur in papermaking systems through the process of sulphate reduction. When the sulphide-containing water is exposed to the atmosphere, most of the dissolved sulphide will be released as H_2S gas, which has a very unpleasant odour and is toxic at low concentrations (occupational exposure limits around 5 ppm). In a normal atmosphere, any sulphide is unstable and may be oxidised to sulphur or back to sulphate, but this reaction is very slow without the mediation of bacteria. Hydrogen sulphide in mill atmospheres can be corrosive directly or after oxidation to sulphuric acid by various species of Thiobacilli bacteria.

Hydrolysate

This is the term for the products of hydrolysis reactions and is most commonly applied in papermaking to the hydrolysis products from AKD and ASA sizes.

Hydrolysis

This term literally means "broken down by water" and occurs when a substance reacts chemically with water. In most situations within papermaking, hydrolysis is an undesirable process as it usually means that the functionality of the additive is impaired, the best examples of this being the incidental hydrolysis of alkylketene dimer and alkenylsuccinic anhydride sizes. However, hydrolysis can be intentional and beneficial as in the case of wet end addition of alum, which hydrolyse to form various cationic complexes and thereby lower the system pH (the latter aspect not always being desirable).

Hydrophile-lipophile balance (HLB)

This term is used to describe the relative proportion of hydrophilic and hydrophobic groups within a molecule. The HLB value is low for hydrophobic substances and increases with the degree of hydrophilicity. In papermaking, it is an important characteristic for sizing agents, surfactants, emulsifiers and some chemicals (such as talc) used for controlling pitch and stickies.

Hydrophilic

This term means that a substance has an affinity for water or can be wetted to some degree by water molecules. It is relevant to the subjects of interfacial energy and surfactants.

Hydrophobic

This term means that a substance has no or little affinity for water and thus cannot easily be wetted by water molecules. Chemicals used in papermaking that have some hydrophobic character are defoamers, sizing agents, surfactants and talc. Some undesirable substances that enter the papermaking system such as pitch and stickies also have some hydrophobic character. Such molecules can form a hydrophobic association (eg micelles for surfactants) to lower their free energy.

Hydroxyl

This important functional group exists in two forms:

- as the hydroxyl ion (OH^-), the concentration of which is related to pH through the ion product for water, K_W.
- as the hydroxyl group (-OH), which is the functional group in alcohols and is present in other organic functional groups (such as carboxylic acids). It is also very important in its own right due to the hydrogen-bonding ability of hydroxyl groups on cellulose and other OH-containing organics such as starch.

Hydroxonium

This is the H_3O^+ ion, which is the stable form of protons in aqueous systems.

Hygro-expansivity

This term refers to the expansion characteristics of materials, notably of hygroscopic fibres in papermaking, under moist conditions. Fibres expand more in their cross-sectional area than in their length when water penetrates the inter-fibril pores and hydrogen bonds with cellulose. As most of the fibres are aligned in the machine direction (MD) in paper, this leads to greater expansion in the MD than CD (cross-direction). The relative MD:CD hygro-expansion is related to the fibril angle, the difference between MD and CD becoming less pronounced as the angle increases.

Hypobromous acid

This acid (HOBr) is generated when either bromine dissolves in water or sodium hypobromite is added to water:

$$Br_2 + H_2O \leftarrow\rightarrow HOBr + HBr \leftarrow\rightarrow Br^- + OBr^- + 2H^+$$

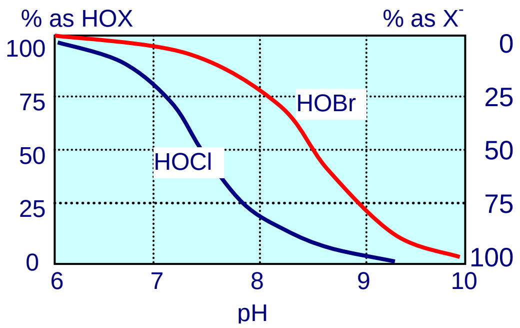
However, it is most commonly generated either from the reaction between sodium bromide and sodium hypochlorite or through the hydrolysis of added halogenated hydantoins. Hypobromous acid is a weaker acid than hypochlorous acid is thus more effective at alkaline pH (see this figure).

Hypochlorous acid

This acid (HOCl) is generated when either chlorine gas dissolves in water or sodium hypochlorite solution is added to water:

$$Cl_2 + H_2O \leftarrow\rightarrow HOCl + HCl \leftarrow\rightarrow Cl^- + OCl^- + 2H^+$$

Sodium hypochlorite is the most common source of hypochlorous acid when it is used in papermaking. Depending on the buffer capacity of the water, this produces a solution of higher pH than chlorine at an equivalent dose (of available chlorine). Hypochlorous acid is a more powerful biocide than the hypochlorite ion (OCl^-). The pK value for the ionisation of HOCl is about 7.5 at 20°C so, as the pH get closer to 8, the available chorine loses some of its biocidal activity as the acid ionises to hypochlorite (see figure at right). Being a weaker acid (pK = 8.5), hypobromous acid ionises less than hypochlorous acid at the same pH and thus maintains more of its biocidal activity under alkaline conditions. This is the main reason why sodium hypobromite has become popular for disinfection of waters above pH 7. An alternative source of hypochlorous acid (and hypobromous acid) is the halogenated hydantoins.



Inks

A very wide range of ink formulations are used for the many different types of printing process, but all contain three ingredients or sets of ingredients:

- the colorant which is a dye or, more usually, a finely-divided pigment (eg carbon black). In the latter case, dispersants are also used to prevent particle aggregation.
- the vehicle, which acts both as a carrier for the ink and also as the binding agent. Organic solvents (eg alcohols, glycols) are the most widely-used, but water-based inks are becoming increasingly popular for commercial-scale flexographic printing and through the use of ink-jet printers. Because of the ink's more hydrophilic character, papers printed in this way are less easily deinked than papers printed with more traditional inks.
- modifiers, which are minor components, but critical to the ink's performance. They can control properties such as drying rate (eg soaps, anti-oxidants), ink transfer (eg lubricants) and scuff resistance (eg waxes).

Inks vary greatly in the way that the applied ink dries:

- absorption, whereby the vehicle (normally an oil) is taken up by the pores in the paper, leaving the pigment behind on the paper surface. This type of ink is used in printing by letterpress, which is typically used for printing newspapers.
- evaporation, whereby the vehicle has sufficient volatility (eg alcohols) to escape into the atmosphere before any absorption takes place. This type of ink is used in letterpress, flexographic, web-offset lithographic and rotogravure printing.
- oxidation, where, after some initial absorption, the unsaturated drying oil oxidises through exposure to air to give a flexible ink finish. This type of ink is commonly used in sheet-fed lithographic printing.
- radiation curing, whereby the exposure to ultra-violet (or infra-red) light initiates a cross-linking polymerisation of what are usually acrylate monomers. These inks are used for printing of magazines and speciality papers.
- heat curing, whereby polymerisation of the vehicle or over-varnish is achieved at elevated temperature. This is used in xerographic and laser printing.

Unless specifically removed in a deinking process, inks will be present in a dispersed state when paper is made and, despite their obvious effect on product appearance, introduce no real problems in terms of process chemistry.

Inorganic chemistry

This is one of the three main branches of chemistry and is defined as the chemistry of the elements and their compounds, including that of elemental carbon, its oxides and metal carbonates. Compared to organic compounds, there are a relatively small number of inorganics used in papermaking:

- minerals used as wet end fillers and coating pigments
- aluminium compounds of various types
- acids such as sulphuric acid
- alkalis such as sodium hydroxide, sodium carbonate and sodium silicate.
- neutral electrolytes such sodium chloride
- oxidising chemicals such as sodium hypochlorite, chlorine dioxide, hydrogen peroxide and oxygen
- reducing agents such as sodium hydrosulphite
- zirconium compounds.

Insolubilisers

These chemicals are used to increase the water resistance of surface-applied materials by reacting with water-soluble materials (eg starch, CMC, proteins) to decrease their solubility in water. This is normally done by a cross-linking reaction that increases the substance's molecular mass. Improved water resistance can also be achieved through simply incorporating water-resistant (ie hydrophobic) materials in the formulation, but this is not genuine insolubilisation. The paper's water resistance is relevant to printing with water-based inks or where water contacts the paper during printing (eg offset litho) and gluing with water-based adhesives (eg corrugated cases). There are a number of possible chemicals used for this purpose:

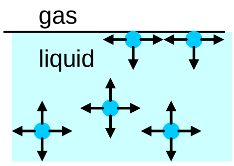
- zirconium salts, which react strongly with oxygen-containing chemicals to form cross-links
- formaldehyde-based chemicals such as formaldehyde itself, glyoxal, MF resins and UF resins
- borates, which are used more in the converting of packaging products (as an adhesive insolubiliser) than in papermaking.

Intensive

This word has a specific meaning in thermodynamics when referring to different properties of the system. An intensive property is one that does not depend on the mass of substance in the system, whilst an extensive property does depend on the mass of substance in the system. For example, the titrated charge demand depends on the quantity of charged substances in the sample that are accessible to the titrating chemical and is thus an extensive property. By contrast, the charge (or strictly, the potential) of a particle is an intensive property because the value does not depend on the number of particles present.

Interfacial energy/tension

This very important concept in surface chemistry is the force acting at the interface between two substances, eg water-fibre and water-air. It is important to the subjects of adhesion, contact angle, wetting and sizing. It is measured either as a tension (in units of force/length, eg N/m) or energy (in units of energy/area, eg J/m^2). The generic term *surface* energy or tension should be reserved for an interface with a gas, but is often used interchangeably with interfacial energy or tension for all situations. However, the surface tension of water always refers to the tension (energy) at the interface with air. This energy/tension is best visualised as the energy required to increase the area of the interface by unit amount.



This surface force results from the imbalance of forces at an interface, ie between the inter-molecular cohesive forces within each material and the inter-molecular adhesive forces between the two materials (see picture at right for the liquid-gas interface). Originally, surface energy was considered to be due to a combination of van der Waals forces and polar forces, but this has been modified in the Lifshitz theory to combine all electromagnetic interactions into one term (Lifshitz-van der Waals component) with an additional component due to acid-base interactions when Lewis acids (electron acceptors) and Lewis bases (electron donors) are present. If the substance can act only as a Lewis acid or a Lewis base, there is no contribution from this second component.

Surface energy, $\gamma = \gamma_{LW} + \gamma_{AB} = \gamma_{LW} + 2(\gamma^{+}.\gamma^{-})^{0.5}$

where γ_{LW} = Lifshitz-van der Waals component , γ_{AB} = acid-base component,
γ^{+} = acid component and γ^{-} = base component

In the case of liquids such as water in contact with air, the surface molecules experience a net attractive force acting inwards, whereby the surface area is reduced in order to minimise the surface free energy. The minimum energy configuration for water droplets in air or air bubbles in water is a sphere as this minimises the surface area/volume ratio. The surface tension of water (in air) is about 73 mN/m (73 mJ/m^2) at 20°C, which is high compared to other liquids and is due largely to the contribution from the Lewis acid/base activity responsible for the hydrogen bonding between water molecules. The interfacial energy between other materials and air is shown in the table above.

Material	Interfacial energy (mN/m) at 20°C
Alkyl ketene dimer	33
Calcium carbonate	76
Cellulose	76
Ceramic press roll	38
Granite press roll	42
Ethanol	29
Kaolin clay	600
Mercury	500
Polyester fabric	45
PTFE-coated polyester	28
Rubber-surfaced press roll	24
Talc	35-68
Water	73

The surface tension of water depends on:

- the nature and concentration of dissolved solids, decreasing when surface active chemicals like detergents are present and increasing, albeit slightly, when dissolved electrolytes are present, eg a 60 g/l solution of sodium chloride raises the surface tension of water by about 2 mN/m.
- its temperatures, decreasing progressively as the temperature rises due to the greater mobility of water molecules and their lower inter-molecular attraction. The surface tension of water is about 65mN/m at 50°C.

Interfering substances

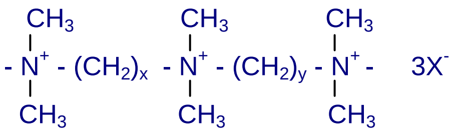
This is a rather loose term that is most commonly used in the same sense as "anionic trash", but it could be argued that all problematic substances interfere with the process/product in some way. Given this uncertainty, it is advisable not to us this term at all, at least not without defining clearly what is meant by it.

Internal sizing

This is an alternative name for sizing at the wet end.

Ionenes

These are low molecular weight cationic polymers that can be used for charge neutralisation. The best-known ionene is probably Polybrene, which is not added to the papermaking system, but is often used to in the standard polymer-based charge titrations to quantify the cationic demand. The generic formula for x, y - ionenes is shown at right where X is the counter ion. Polybrene is a 3,6-ionene of molecular weight 8K Daltons and charge density 5.5 meq/g with bromide as the counter-ion.



$$-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N^+}} - (CH_2)_x - \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N^+}} - (CH_2)_y - \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N^+}} - \quad 3X^-$$

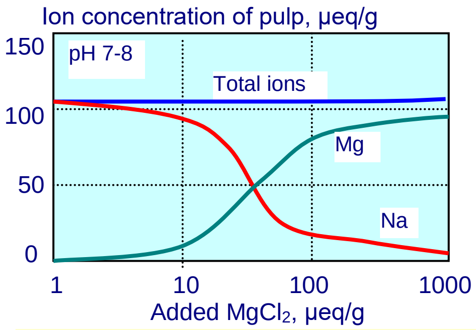
As the molecular weight of these polymers is not high, commercial products are usually available as solutions having a solids content of about 20-40%. Doses are dictated by the cationic demand in the system, ranging up to about 2 kg/tonne paper.

Ion exchange

This is the process whereby a charged particulate surface (eg an anionic fibre or filler) replaces its associated cation with another in the light of the relative concentrations of cations in the surrounding liquid. In a situation where the surface anion or cation cannot move (eg some anionic hemi-celluoses in pulps), the distribution of ions in the liquid phase is determined by the Donnan equilibrium. In the case of papermaking pulps, the thickened or dried pulp contains an electrolyte content depending on the water chemistry in the final pulping or bleaching stage at the pulp mill. The cations with the pulp are likely to be a mixture of sodium and calcium ions rather than hydrogen ions.

When the pulp is slushed with water at the paper mill, the chemistry of the liquid phase will almost certainly be different and a new equilibrium will establish itself. The balance of cations associated with the anionic charges on the pulp is important as this influences fibre swelling (and hence the pulp's strength potential) and the adsorption of additives (see this example for a cationic polyacrylamide). The most likely shift in cation balance from pulping to papermaking is that there will be a higher level of divalent cations (calcium and magnesium) compared to monovalent sodium.

Such a change is shown at right for an unbleached softwood Kraft pulp that has an anionic group content of 106 µeq/g and fibre saturation points of 1.15 g water/g pulp in the Na$^+$ form and 1.1 g water/g pulp in the Mg^{2+} form. It is evident that, when the amount of divalent cation is the same as the anionic content of the pulp (ie at about 100 µeq/g added Mg^{2+}), about 80% of the cation within the fibre wall is in the Mg^{2+} form. It can be calculated that, at a pulp concentration of 10 g/l, the concentrations of Mg^{2+} and Na$^+$ in the fibre wall water are about 1000 and 100 mg/l respectively compared to about 10 mg/l for both in the bulk solution. The total concentrations of Mg^{2+} and Na$^+$ (when averaged across the total water present) are about double these levels, ie 20 mg/l. It is likely therefore that, as the concentration of divalent cations (usually Ca^{2+} rather than Mg^{2+}) is higher than monovalent cations such as Na$^+$ in most papermaking systems, the pulp's anionic groups will be associated with divalent cations.



Source: Laivins and Scallan in Transactions 11th FRS, Cambridge, 1997, 837-857.

Ionic bonds

These are one of the three types of chemical bond, this case being where the bonding electrons are transferred from one atom to another and the two ions are then held together by the strong electrostatic attraction between them. The best examples are electrolytes such as sodium chloride (Na$^+$Cl$^-$). The ability of atoms to gain or lose electrons depends on their electronic configuration as this determines their ease of accepting or donating electrons, ie their electrophilic or nucleophilic character. In the solid phase, ionic compounds are often crystalline with the actual structure being dependent mainly on the relative size of the two ions and their relative numbers. For example, sodium chloride (rock salt) has an octahedral structure in which each anion and cation is surrounded by 6 ions of opposite charge. In titanium dioxide (rutile form), the titanium ion is also surrounded by octahedral oxide ions, but the oxide ions are surrounded by only 3 titanium ions and have trigonal planar structure.

Ionic strength

This is a measure of the strength of ions in solution and is calculated as follows:

I = ionic strength = $\frac{1}{2}\Sigma c_i.z_i^2$ where c_i= ion concentration and z_i = charge of the ion

As is evident from the above, multi-valent ions contribute proportionately more to the ionic strength than they do to their mass concentration eg a 0.001M solution of calcium bicarbonate (100 mg/l as $CaCO_3$) has an ionic strength of 0.003M. The ionic strength is used in the calculation of ion activities and the thickness of the electrical double layer that surrounds charged particles. It is not measured directly or calculated in papermaking, but its influence is normally evaluated via measurement of conductivity.

Ions

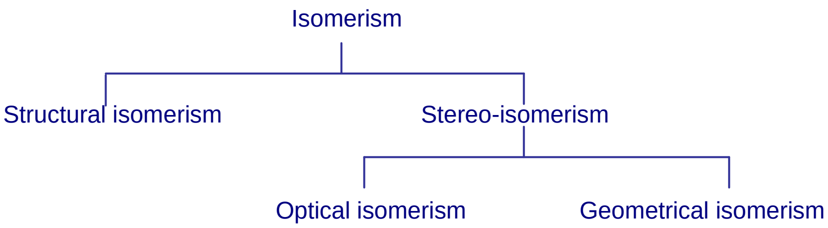
An ion is a charged atom (eg Na^+ for sodium and Cl^- for chloride) or charged molecule (eg SO_4^{2-} for sulphate and HCO_3^- for bicarbonate). Negatively-charged ions are anions and positively-charged ions are cations. Simple ions like this are responsible for the ability of water to conduct electricity. For charged atoms, cations tend to be smaller than the parent uncharged atom due to the greater pull of the nucleus on the remaining electrons and, conversely, anions tend to be larger than the uncharged atom. Because of this, for isoelectronic atoms (ie those with the same number of electrons), the cation is always smaller than the anion, eg both Na^+ and F^- have the electronic configuration $1s^2$, $2s^2$, $2p^6$, but the sodium ion has a radius of just under 0.1 nm compared to about 0.14 nm for the fluoride ion.

The presence of ions within the liquid phase in papermaking systems is often not fully appreciated, but is very important for many reasons which are discussed further under electrolytes.

Isoelectric point

This is the pH when the charge on a particulate surface is zero. For example in the case of pulp fibres, the isoelectric point is about pH 2.5 when the acidic groups within the anionic hemi-celluloses become fully protonated (see the graph here) and fillers also have their own characteristic point of zero charge (see the graph here). The pH in papermaking systems is always above the isoelectric point for pulps and is reasonably stable at typical papermaking pH levels in the neutral range (pH 6-8).

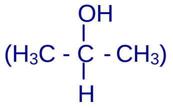
Isomers



Isomerism is exhibited by organic chemicals that have the same formula, but different forms and, as shown above, there are three different types of isomerism. Compounds with the same molecular formula can have different chemical structures and hence different chemical characteristics. A simple example is propanol (C_3H_8OH), which can exist in the two forms shown at right. These two forms are structural isomers, but, both being simple alcohols, are not that different chemically. By contrast, the molecular formula C_2H_6O can be written as an alcohol (C_2H_5OH, ethanol) or as an ether (H_3C - O - CH_3, dimethyl ether), which are very different chemically.

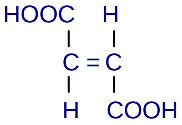
1-propanol $H_3C - CH_2 - CH_2OH$

2-propanol (iso-propanol)

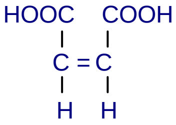


$(H_3C - \overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}} - CH_3)$

Another form of isomerism is stereo-isomerism, where the structures are identical, but the spatial arrangement is different, ie they have different configurations. There are two forms of this, the simpler being geometrical isomerism which is also referred to as cis-trans isomerism. This only applies to structures with double bonds where, because of the π-bonds (see valency), no rotation about this bond is possible. A good example is two chemicals which can be used to fortify rosin size - maleic acid (or its anhydride) and fumaric acid, the formulae of which are shown at right. Fumaric acid (left-hand side) is the trans-form and maleic acid (right-hand side) the cis-form. The unsaturated fatty acid, oleic acid, is in the cis-form and is used to make alkenylketene dimers. The isomeric form of fluorescent brighteners is important to their functionality.



$$\begin{matrix} \text{HOOC} & & \text{H} \\ | & & | \\ \text{C} & = & \text{C} \\ | & & | \\ \text{H} & & \text{COOH} \end{matrix}$$



$$\begin{matrix} \text{HOOC} & & \text{COOH} \\ | & & | \\ \text{C} & = & \text{C} \\ | & & | \\ \text{H} & & \text{H} \end{matrix}$$

The most complex form of isomerism is optical isomerism, where the molecule has no symmetry and can therefore rotate the plane of polarisation of plane-polarised light. This is present in many carbohydrates present in papermaking systems and is discussed further under monosaccharides.

Joule

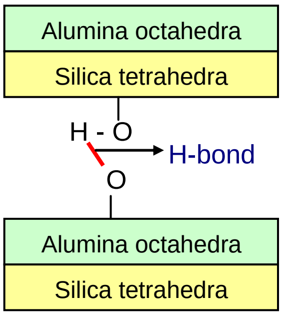
This is the basic unit of energy or work and is usually abbreviated J where 1 J = 1 Newton.metre (N.m) = 1 $\text{kg.m}^{2}.\text{second}^{-2,}$, ie it is the work done by a force of one Newton acting to move an object through a distance of one metre in the direction in which the force is applied.

K

This is an abbreviation either for Kelvin degrees (absolute temperature scale) or the element potassium.

Kaolin clay

Kaolin clay used to be the dominant mineral type for filling and coating applications globally, but today it shares this market on an approximately equal basis with calcium carbonate. The name of this clay is derived from the deposits in China, but the main source of kaolin clays for papermaking has been the enormous deposits in south west England. However, this source is decreasing as a proportion of the world total due to the exploitation of deposits elsewhere. The UK deposits are primary clays as they are still present as part of the original igneous rock matrix, whereas many of the other deposits (eg in Georgia, USA and in Brazil) are secondary sedimentary deposits, which have been transported by water (and therefore partially purified). Only about 10% of the primary deposits are kaolin clay, whereas the secondary deposits are at least 90% clay. All clays are purified by a series of largely mechanical classification steps to remove impurities and produce products of defined particle size distribution. Chemical treatment with sodium hydrosulphite can be used to enhance brightness through dissolution of iron impurities.



Chemically, kaolin clay is an alumino-silicate with the formula $Al_2Si_2O_5(OH)_4$ and the structure as shown in a simplified form at right. The alumina and silica layers are tightly bonded, but the paired layers are held together by much weaker hydrogen bonds. The individual hexagonal clay plates are less than 1 nm thick. Because of their flat, platy structure, clay-filled papers are smooth with a good printing surface and give the paper a good response to calendering. The platy structure also accounts for the high gloss of clay coatings, its relative softness (Moh scale 2) and low abrasion characteristics. The density of clays is 2.6 kg/dm^3 and refractive index 1.58, but the main papermaking properties of clay fillers vary with each of the three broad categories as summarised below.

Filler	Brightness (ISO, %)	Light scattering Coefficient (m^2/kg)	Particle size distribution (%)				Surface area (m^2/g)
			+10µ	-2µ	-1µ	-0.5µ	
Coating clay	85-88	-	0	80	60	40	14
Filler clay	82-88	120-160	10-30	17-60	5-30	1-5	6
Calcined clay	90-92	260-340	0-10	40-80	25-90	15-80	10-22

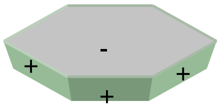
As the individual hexagonal clay plates are less than 1 nm thick, the actual particles used in papermaking are assemblages of many individual plates in which the aspect ratio (length:thickness) can be engineered for different applications. The primary clays have a highly variable aspect ratio (10:1 to 80:1) depending on the processing conditions, but it tends to increase as the particle size is reduced. The aspect ratio of secondary clays is lower (6:1 to 20:1), but, in this case, it tends to decrease as the particle size is reduced.

Delamination of coarse clays by special grinding processes produces clay platelets of relatively high aspect ratio (6-8 times that of normal clays) with enhanced light scattering power. Specific structuring of the clays occurs when clay is calcined at high temperature, thus removing the water and causing the platelets to fuse in a face-to-face configuration. This produces a bulky clay with a high internal void content (about 1 cm^3/g) and thus excellent light scattering ability (see table above). Chemical structuring of clays is achieved by flocculation, usually with cationic polymers. Although these products are less effective opacifiers, they do have the useful attribute of a lesser adverse impact on paper strength.

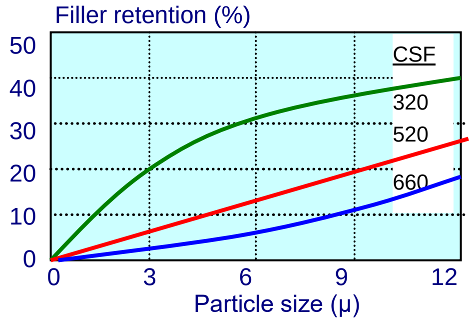
Although kaolin clay usually has a negative zeta potential under normal papermaking conditions, it does have some dual charge character due to the differences between the alumina and silica groups. The overall negativity is usually attributed to isomorphous substitution within the lattice structure, whereby trivalent aluminium takes the place of tetravalent silicon at some positions. Charges also occur due to ionisation of surface oxides/hydroxides:

$$- MOH_2^+ \xleftarrow{H^+} - MOH \xrightarrow{OH} - MO^- + H_2O$$

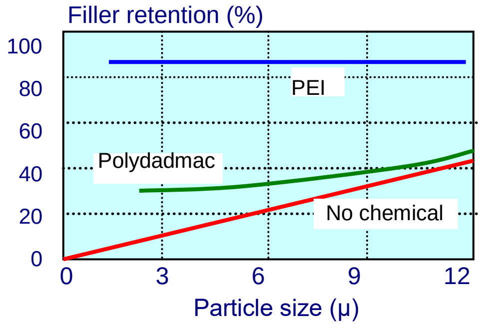
The silanol groups (M = Si) on the silica plate surface give rise to negative charges above pH 2 and the aluminol groups (M = Al) on the alumina edge surface gives rise to a positive charge below pH 9. These surface charges give clay some anion and cation exchange capacity, the two being of about the same order of magnitude at pH 5, the isoelectric point for clay. The ion exchange capacity of kaolin clays thus depends on pH, but is up to about 0.01 meq/g for anions and up to about 0.1 meq/g for cations (lower than bentonite and higher than talc). The dual charge character leads to a natural edge-face flocculation at neutral pH, leading to what is commonly referred to as a "house of cards" structure (see bentonite), but this is relatively weak.



Retention of clay fillers has been shown to depend to some degree on their particle size, but only in the absence of retention chemicals. This is shown in the two figures at right for 60 g/m^2 laboratory handsheets made using clays with narrow particle size distributions. In the absence of retention aids, increased refining of the pulp improves filler retention through enhanced filler deposition on pulp as the pulp surface area increases. When the filler dose is increased with a particular pulp, filler retention remains stable until a threshold dose is reached, after which it declines due to there being inadequate pulp surface area for filler deposition. Under these circumstances in the absence of any retention polymer, filler retention is solely due to non-electrostatic attractive forces between pulp and filler, which would be too weak to withstand the shear forces on most paper machines. Under more realistic papermaking conditions with a retention chemical present, any dependence of retention on particle size is effectively removed when efficient retention aids are used. This is shown in the lower figure at right for optimum levels of two retention polymers, the filler retention being consistently high with polyethyleneimine.



Source: Bown in Paper Technology, 1990, 31, 4, 20-27



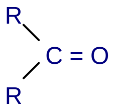
For the coating clays, the bulk void volume of the compacted (settled) clay suspension is important as, together with the particle size distribution, this determines the binder demand.

Kappa number

This is standard test applied to pulps as an index of their lignin content, but it is normally only done on chemical pulps as there is no deliberate lignin removal in mechanical pulping. It involves treating the pulp with a standard solution of potassium permanganate ($KMnO_4$), which oxidises the lignin. The Kappa number is simply the volume of 0.1N KMnO4 (in millilitres) that is reduced by 1g of dry pulp. Values range from above 100 for unbleached chemical pulps down to 20-30 for unbleached pulps intended for bleaching. Examples are given here for the relationship between the anionic group of Kraft pulps and their Kappa number and here for the similar relationship with sulphite pulps.

Ketones

These are organic compounds containing the carbonyl group linked to two carbon atoms (as shown at right). They are produced by the oxidation of secondary alcohols. Ketones themselves are not present in any significant papermaking chemicals, but alkylketene dimer does produce a keto-acid and/or ketone on hydrolysis.



Kinetics

In chemical terms, this is the study of the rate of chemical reactions or, more generally, interactions. The thermodynamic aspects of such interactions determine whether or not it is likely or possible to take place, but kinetic aspects determine whether it actually does take place within the timeframe available. Chemical reactions rarely occur deliberately at the wet end, but many do so incidentally, nearly always leading to various problems. Intentional chemical reactions are more common during the drying process where they are driven by the high sheet temperatures. The main examples are the curing reactions to maximise the functionality of AKD and ASA sizes and of wet strength resins. Kinetic theory can also be applied to simple interactions such as the collisions between particles that may lead to particle aggregation.

The rate of a chemical reaction is dependent on many factors, notably the concentrations of reacting species, temperature, pressure where gases are involved and the presence of catalytic substances. Reaction rates are usually described in terms of their order of reaction:

- first order reactions: A → products where $-d[A)/dt = k_1[A]$

where on integration, $\ln [A_t]/[A_0] = kt$ or $[A_t] = [A_0]e^{-kt}$

where $[A_t]$ = concentration of A at time t and $[A_0]$ = initial concentration of A
and k_1 = first order rate constant

This states that the concentration of A decreases exponentially with time.

- second order reactions: A + B → products where $-d[A)/dt = ko[A][B]$

or A → products where $-d[A)/dt = k_2[A]2$

which on integration gives $(1/[A_t]) - 1/([A_0]) = k_2t$ where k_2 = second order rate constant

In nearly all situations, reaction rates increase with raised temperature and this relationship takes the following form, which is the so-called Arrhenius equation:

$$\text{Rate constant, } k = A\,e^{-E^*/RT}$$

where R = gas constant ,T = temperature (^{o}K), A = frequency factor and E* = activation energy.

The frequency factor and activation energy can easily be calculated from measurements of the rate constant at different temperatures.

Kraft pulps

These pulps are now the most important type of chemical virgin pulp world-wide. The name "Kraft" is derived from the German word for "strong", which is one of the most important characteristics of these pulps. They are also called sulphate pulps, which refers to the use of sodium sulphate as one of the main cooking chemicals, although its active form in the cooking process is sodium sulphide. The Kraft process was developed from the soda process and was used commercially for the first time in Sweden towards the end of the 19th century. With the demise of sulphite pulping from the middle of the 20th century, it has since become the dominant chemical pulping process.

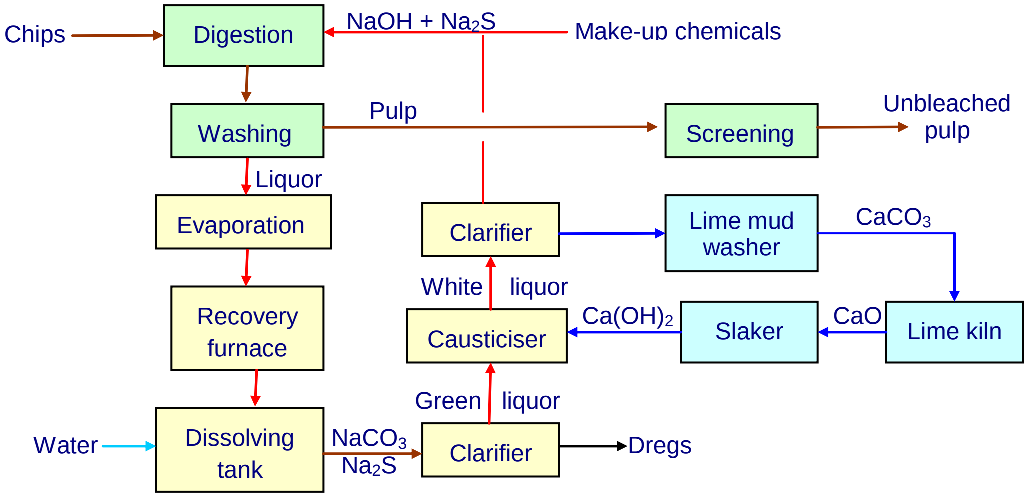
There are two broad categories of Kraft pulp:

- unbleached Kraft pulps made largely from softwoods and used predominantly in linerboard packaging grades
- bleached Kraft pulps made from both softwoods and hardwoods and used in many paper grades, notably in all types of graphical papers, some packagings and tissue. There is also an intermediate grade of pulp known as semi-bleached Kraft, but this is not produced in large quantities.

Kraft pulping is carried out at high pressure/temperature in the presence of sodium hydroxide and sodium sulphide, their total and relative doses being adjusted to maintain the desired alkalinity and sulphidity values. The process conditions and extent of cooking are set to produce a pulp with a target Kappa number, which varies with the type of pulp being made:

- Kappa number of 40-120 (corresponding to a total yield of 45-60%) for unbleached pulps
- Kappa number of 20-30 (corresponding to a total yield of 40-45%) for pulps destined for bleaching.

Kraft pulps to be used for chemical manufacture (dissolving pulps) usually have a pre-hydrolysis phase to maximise the removal of hemi-celluloses. There are many important operational differences between the various types of continuous or batch Kraft process, which are outside the scope of this document. A common feature of all Kraft processes is the chemical recovery operation, which firstly concentrates the black liquor containing the dissolved wood substances by evaporation and then burns the concentrate in a special furnace using the wood-derived organics as fuel (see diagram below).



This energy is recovered and the residual inorganic smelt dissolved to form a solution of sodium carbonate and sulphide. The carbonate is converted back to the hydroxide by re-causticisation with lime, which is itself recovered by calcination of the calcium carbonate. The overall efficiency of this recovery operation at modern, state-of-the-art Kraft mills is reflected in the low figures for auxiliary fuels (sometimes negative) and make-up caustic soda and salt-cake (sodium sulphate).

In Kraft pulping, the lignin is solubilised through destruction of the ether linkages that join the phenylpropane units together and methanol is released from cleavage of methoxy (-OCH_3) groups. Significant formation of carboxyl groups occurs, possibly via disproportionation of aldehyde groups, but these entities dissolve in the liquor and are not retained with the pulp. The hemi-celluloses are easily deacetylated under alkaline conditions to free the hemi-cellulose hydroxyl group and acetic acid. A very important reaction is the end-peeling reaction of the carbohydrates, whereby monosaccharide units are removed from the reducing end of the chain. Under alkaline conditions, the end nearest the ring oxygen isomerises to the keto form followed by cleavage of the glycosidic link between this unit and the adjacent monosaccharide. The released ketone breaks down further to various aliphatic hydroxy and keto carboxylic acids. The peeling reaction can be stopped by formation of carboxyl groups in the metasaccharinic acid end groups, giving a low degree of anionic character to the residual carbohydrate.

The end-peeling reaction affects both cellulose and the hemi-celluloses, but to differing degrees. In normal Kraft pulping, the loss of cellulose through this reaction has been estimated at about 10%, but is greater when pulps are cooked to low Kappa numbers (unless protecting measures are taken, such as the addition of anthraquinone to the cooking liquor). Cellulose is also depolymerised randomly along the chain, albeit mainly in the amorphous regions, through alkaline hydrolysis of the glycosidic bonds, resulting in a chain length of only 1000-1500 units. This reaction is much more significant to pulp strength than end-peeling. In softwoods, the glucomannans dissolve readily during Kraft pulping, whereas the dissolved xylans tend to re-adsorb during the later stages of the digestion; the net result is that the Kraft pulp contains similar amounts of glucomannan and xylan. Some of the glucuronoxylans are converted to hexenuronic acids, which has important implications for bleaching. The final composition of unbleached Kraft pulps is 20-30% hemi-cellulose (highest in hardwoods) and 4-7% lignin (highest in softwoods).

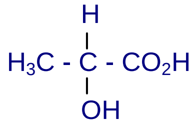
After cooking, the pulps are thickened/washed to remove the residual dissolved substances and then screened to remove shives (over-sized fibre bundles). The washing stage is particularly important for minimising the carry-over of dissolved solids either to the paper machine or the subsequent bleaching stages. Characteristics of unbleached Kraft pulps are described here and of bleached Kraft pulps and bleaching processes here.

Kubelka-Munk Theory

This theory addresses the relationships between transmitted, absorbed and reflected light when light is incident on a hard surface. It was originally developed for paint films, but can be applied to paper. From this theory, the reflectance of paper can be calculated from the measured light absorption and light scattering coefficients. It plays an important role in considering the optical properties of paper.

Lactic acid

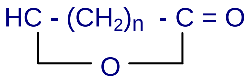
This is an organic acid present in some papermaking systems due to the ctivity of anaerobic bacteria. It is a hydroxy-carboxylic acid with a central asymmetric carbon atom and the formula shown here.



$$H_3C - \overset{H}{\underset{OH}{C}} - CO_2H$$

Lactones

These are organic compounds which are often referred to as internal esters. They are cyclic compounds with the general formula shown at right. There are no lactones with n = 0 due to steric constraints, but the higher lactones are termed β-lactones when n = 1, γ-lactones when n = 2 and δ-lactones when n = 3. There is one papermaking chemical containing a lactone ring and this is alkyl ketene dimer size.



Langelier's equation

The pH of water is determined by the balance of acidic materials such as humic acids from peat and carbon dioxide against alkaline materials such as calcium carbonate. In the absence of peat-derived acids or mineral acidity, the following equilibria determine the pH:

$$H_2O + CO_2 \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^- \leftrightarrow H^+ + CO_3^{2-}$$

$$HCO_3^- + Ca^{2+} \leftrightarrow CaCO_3 + H^+$$

One of the important issues for water supplied into a distribution system is its stability towards the precipitation or the dissolution of calcium carbonate. This can be calculated from Langelier's equation, where a water at the saturation pH has no tendency to precipitate or dissolve calcium carbonate:

$$\text{saturation pH, } pH_s = -pK + pCa + pAlk$$

where Alk = dissolved bicarbonate alkalinity (mole/l)
and Ca = calcium concentration (mole/l)

The K value is the equilibrium constant for the second equation above. At 25°C, pK = -2, but, as with all such "constants", it does vary with temperature and also needs to be modified for the effects of other electrolytes on ion activities. If the actual pH is above the saturation pH, then the water will tend to precipitate calcium carbonate, whereas any carbonate scale would be dissolved when the saturation pH exceeds the actual pH.

The Langelier equation is applicable only to closed systems where the carbon dioxide does not equilibrate with the CO_2 level in the atmosphere. This reflects the fact that it was developed in the context of potable water supply, where the distribution system is closed to the outside atmosphere. The main concern in such systems is the prevention of corrosion so the water quality should ideally be optimised to precipitate a small amount of calcium carbonate as a surface scale to protect the pipework from other corrosive substances such as chloride ions.

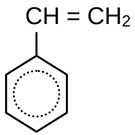
Just for illustration, the big difference between such systems can be appreciated by looking at the solubility of calcium carbonate. In a system closed to the atmosphere at 25°C, its solubility is about 13 mg/l (as $CaCO_3$) giving a pH of 9.9, whereas the solubility is about 50mg/l (as $CaCO_3$) with a pH of 8.4 in a system open to the atmosphere at 25°C. The presence of the electrolytes increases the solubility so that dissolved levels of 100 mg/l ($CaCO_3$) could be seen in some papermaking systems. It is not common to see Langelier indices quoted for paper machine waters, but some values are quoted here for several machines with fully-closed water systems.

Latency

This term is applied to mechanical pulps, notably TMP pulps, which become deformed at high consistency where the fibres curl and twist around one another. This leads to increased freeness and low strength and efficient screening becomes difficult if not impossible. Latency is therefore removed from such pulps prior to screening by agitation at low consistency (2-4%) and high temperature (70-80°C) in 1 or 2 stages.

Latex

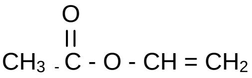
This term is traditionally associated with an emulsion of natural rubber particles, but it can be used more generally for any emulsion or dispersion of natural or synthetic polymers having similar functions or properties. In papermaking, latices are used mainly as binders in conventional aqueous pigment coating of paper, but they can also be used as barrier coatings and to confer wet strength through wet end addition. They are all made by the process of emulsion polymerisation in which the monomers are firstly suspended in water and polymerisation initiated by water-soluble free radicals (eg persulphate salts). The main monomer building blocks are shown here:



Styrene

$CH_2 = CH - CH = CH_2$

Butadiene



$CH_3 - \overset{\overset{O}{\parallel}}{C} - O - CH = CH_2$

Vinyl acetate

$CH_2 = CH - CO_2R$

$R = CH_3$ is methyl acrylate
$R = C_2H_5$ is ethyl acrylate

Small amounts (up to 10%) of modifiers (unsaturated carboxylic acids such as fumaric or methacrylic acids and unsaturated amides such as acrylamide) may be added to improve key latex characteristics such as adhesion and film formation and, possibly with added surfactants, also to control its colloidal stability. The presence of carboxylic acid groups in these modifiers gives rise to the term "carboxylated latices". The diameter of the spherical latex particles is typically 0.1-0.3 μm with a solids content of around 50%. The commercial products may also contain foam control agents and biocide.

Latices are the main type of coating binder, but are most commonly used in conjunction with a co-binder such as starch, PVOH, etc, which, although having a lower binding power, are able to control the rheological characteristics of the coating mix. Latices also have the advantages of being supplied in a ready-to-use form and can be stored without fear of microbiological breakdown. The main latices used as coating binders are:

- styrene-butadiene (SB) co-polymers, which are the most widely-used type
- styrene-acrylate (SA) co-polymers
- polyvinyl acetate (PVA) homo-polymers

Characteristics of latices that are important to their selection for a particular application are:

- their glass transition temperature, which affects the physical nature (flexibility) of the latex
- their minimum film formation temperature
- their interfacial energy, which is important in relation to the wetting of and adhesion to the base paper and to the printability of the coated paper
- their particle size distribution with smaller particles generally improving binding power, but also increasing latex viscosity.

Light absorption

When light is absorbed, the absorbing material takes on the colour of the transmitted light. This is important in relation to the overall optical properties of paper and the use of dyes and pigments. In the Kubelka-Munk theory, a light absorption coefficient is defined as follows:

$$\text{Light absorption coefficient} = \lim_{G \to 0} \left[\frac{\text{energy of absorbed light}}{\text{energy of incident light x grammage (G)}} \right]$$

The coefficient is typically below 2 m^2/kg for coated and uncoated fine papers made from bleached chemical pulps, 3-6 m^2/kg for mechanical pulps and around 14 m^2/kg for unbleached Kraft pulps.

Light scattering

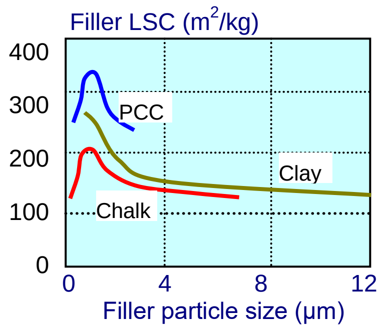
Light is scattered when it changes direction due to reflection at an interface and this is important to the opacity and other optical properties of paper. The light scattering of paper is determined by a combination of the sheet structure and the optical properties of the component materials. In the Kubelka-Munk theory, a light scattering coefficient is defined as follows:

$$\text{Light scattering coefficient} = \lim_{G \to 0} \left[\frac{\text{energy of reflected light}}{\text{energy of incident light x grammage (G)}} \right]$$

The units for the coefficient are reciprocal grammage, ie m^2/g or, more commonly, m^2/kg.

Material	Light scattering coefficient (m^2/kg)
Mechanical pulps	50-80
Chemical pulps	20-40
Chalk	150
PCC, scalanohedral	220-290
Kaolin clay	120-160
Calcined clay	260-340
UF pigments	450
Titanium dioxide	550-600

The light-scattering coefficients for various materials are shown in the table at right. It should be noted that the filler values are apparent, not absolute, values, as they depend on the fibrous environment, the state of association of fibre/filler and the degree of sheet consolidation. Provided that there is no interaction when components (eg fibre and filler) are combined, the apparent filler scattering coefficients can be calculated on the assumption that the paper's light scattering coefficient is simply the proportional sum of the fibre and filler coefficients. However, this is almost certainly not true in practice due to the debonding effect of the filler and the increased fibre surface available for light scattering when filler is present.



Source: Bown in Transactions 11th FRS, 1997, 83-137.

For normal white fillers, in which light absorption is low, the light scattering coefficient is the main vehicle for their opacifying effect. The actual light-scattering power of fillers is dependent on a combination of their refractive index and morphological characteristics such as particle size, shape and void structure. Theoretically, maximum light scattering for spherical particles occurs at a particle size of about half the wavelength of the incident light (ie 0.2-0.4 µm for visible light). Because of the importance of other factors for non-spherical particles, a somewhat higher optimum particle size is usually observed, as shown at left for the three commonest types of papermaking filler.

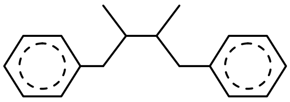
Light-weight coated paper

This is the premium grade of wood-containing paper due to its coated surface. The grade structure of LWC papers is broken down solely in terms of grammage with the coated product spanning the range 45-70 g/m^2, but there is also a heavier-weight range up to about 120 g/m^2, which are called medium-weight coated (MWC) papers. For the LWC grades, the base paper has a grammage of 35-45 g/m^2 and the coating contributes a further 6-12 g/m^2 on each side. Brightness levels cover the range 70-78% on the ISO scale.

The base paper is normally made from an approximately equal mixture of mechanical pulp and bleached Kraft pulp with coated broke providing most of the filler in the base paper. Kaolin clay has traditionally been the coating pigment, but calcium carbonates are also now being used. Over the last 10 years or so, deinked pulp has also begun to be used to replace the virgin pulps so that a typical pulp blend could be equal quantities of mechanical, chemical and deinked pulps. Like newsprint and SC paper machines, LWC paper machines are very fast (up to just over 1800 m/minute) and provide an equally challenging environment for retention aids. The recycle of coated broke provides an additional source of anionic trash from pigment dispersants and there is potential for additional pitch problems from latex-derived white pitch.

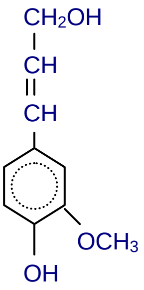
Lignan

This term is used to describe the derivatives of the fundamental unit in lignins, which is that between two phenylpropane units as shown at right. This structure itself is called lignane when the linkage is between the carbon atoms numbered 8 (as shown). When the two phenylpropane units are joined by other linkages, the parent compound is called a neolignane and the derivatives neolignans.

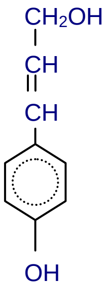


Lignin

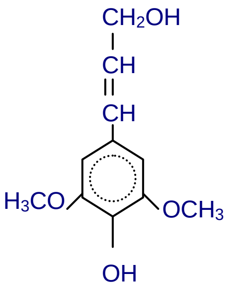
This is the fraction of plant tissue that is responsible for holding the fibres together in a stiff matrix. The lignin content is higher in softwoods (26-32%) than hardwoods (20-25%). In wood (softwood tracheids), its concentration is greatest in the middle lamella, which is virtually 100% lignin, declines through the primary wall and is lowest in the S2 layer. The chemistry of lignin is based on linked phenylpropane units (lignans) as the three building blocks (coniferyl alcohol, p-coumaryl alcohol and sinapyl alcohol) are all hydroxy or hydroxy and methoxy (-OCH$_3$) derivatives of this unit as shown below. In lignin, they are joined together by C-C and C-O-C (ethers) bonds. Lignin is not soluble in water, but can be solubilised by chemical treatment with sulphite and sulphide ions during chemical pulping. It is often measured as so-called Klason lignin, which is the residue after treating the sample (free of extractives in the case of woods) with 72% sulphuric acid.



Coniferyl alcohol



p-coumaryl alcohol



Sinapyl alcohol

The presence of lignin compounds in papermaking pulps has an adverse effect on fibre strength due to physical interference with inter-fibre hydrogen bonding and due to inhibition of fibre swelling. The latter aspect leads to less conformable fibres and reduced sheet bonding, but it does mean that pulps with high native lignin content do drain more easily. Residual lignin compounds in pulps can also be oxidised photo-chemically during exposure to light and this causes the fibre to darken. This tendency increases with pH and is one reason why papers with a high mechanical pulp content tend to be made at a slightly acid pH. In mechanical pulps, lignin is present largely in its natural insoluble state and thus does not contribute significantly to the dissolved solids on the paper machine. With chemimechanical pulps pre-treated with sodium sulphite, the lignin is partially sulphonated and thus dissolves at the wet end, the extent of dissolution increasing with temperature as shown here. The lignin residues in full chemical pulps will have been changed to a more water-soluble form, such as the lignosulphonates formed in sulphite pulping. Kraft lignin, which is present mainly in unbleached pulps, tends to precipitate under acidic conditions, as shown in this example from a linerboard machine.

Lignosulphonates

These compounds are formed in sulphite pulping and in chemimechanical pulping processes that use sodium sulphite for pre-treatment. Lignosulphonates have a high anionic charge (typically about 2 meq/g solids), which can, depending on the efficiency of pulp washing, contribute significantly to anionic trash on the paper machine, thus impeding the efficacy of cationic additives as shown here for polyethyleneimine, here for PAE resin, here for polyacrylamide and here for rosin. This adverse effect is greatest for NSSC pulps due to the difficulty in washing these pulps.

Lime

This is the common name for calcium oxide (CaO, quicklime) or calcium hydroxide - $Ca(OH)_2$, slaked lime. Lime is not used directly in papermaking, but is used in the Kraft pulping process and in the manufacture of precipitated calcium carbonate.

Limestone

This is one of the several different natural forms of calcium carbonate, the mineral widely used as a wet end filler or paper coating pigment. Limestone is a natural form of precipitated calcium carbonate as this is how it was formed in sea water, but it may also contain calcium carbonates from dead plant/animal life-forms. Limestone carbonates are harder than chalk carbonates

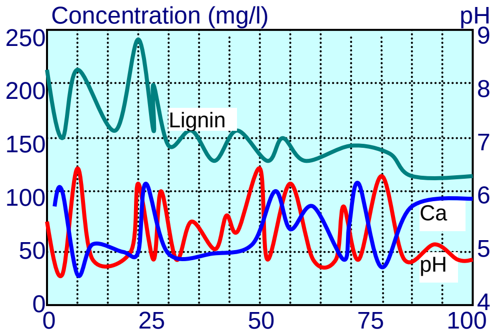
Linerboard

Linerboard is the outer layer in corrugated cases and is the single largest category within packaging papers/boards. There are two distinct types depending on the type of pulp used - linerboard made from 100% unbleached Kraft pulp and linerboard (known as test liner) made from 100% recovered paper, but there are also grades made with blends of these two pulps. Because of the increasing use of the outer surface of the corrugated case to convey information, some linerboard is made with a higher quality, whiter pulp (often a deinked pulp rather than a bleached chemical virgin pulp) to form the outer ply. Apart from the pulp, the main functional wet end additive is size (rosin or AKD), although sizing can be done solely at the size press, but this is not common. Wet end starch may be used to enhance strength depending on the furnish composition. As some corrugated cases are used under wet or moist conditions, wet strength resins may also be added at the wet end. Recycled liner is normally made from recovered corrugated case materials and normally requires the use of some starch to achieve the required strength. As the addition rates are lower than the levels required for recycled fluting, this is normally done by wet end addition.

Linerboard is made in a very wide grammage range (110-450 g/m^2) with the standard linerboard being 205 g/m^2. It is usually made as a duplex product on a paper machine either with a primary and secondary flowbox on the same forming fabric or on two separate Fourdriniers. Key properties are stiffness and burst strength combined with good appearance and printability on the top side. Consequently, two slightly different furnishes are usually used, a cleaner (lower yield) pulp for the top surface with a higher yield, darker pulp underneath. The fines distribution within each ply is particularly important to achieving a good ply bond, the ideal situation being to have two fines-rich surfaces at the ply interface.

Both the virgin pulp-based and recycled grades are made on paper machines with substantially and, in some cases, fully closed water systems. At virgin pulp-based linerboard mills, there is thus a strong incentive to minimise carry-over of pulping-derived dissolved solids in order to minimise build-up problems at such high levels of water closure. The dominant inputs of dissolved solids are residual pulping chemicals and dissolved organics, the following ranges having been quoted for a machines with "open" and "closed" water systems:

- inorganic electrolytes giving 2.5 -15 mS/cm conductivity with concentrations of 400-5000 mg/l sodium ions, 450-900 mg/l sulphate, 20-130 mg/l calcium ions and 150-300 mg/l chloride.
- organic substances with a DOC level of 200-10,000 mg/l and a lignin concentration of 50-1000 mg/l.



Source: Sjostrom at EU COST E14 Conference, England, 1997 .

The variability of three parameters on a Kraft linerboard machine using about 20% recycled pulp is illustrated at right. The machine was running alum/rosin sizing at about pH 5, but the pH was deliberately varied over the range shown (4.8-6.5). It is evident that both the soluble calcium and soluble lignin were correlated with the changes in pH, the calcium negatively (ie high pH leads to less dissolved calcium) and the lignin positively (ie low pH leads to low dissolved lignin).

This confirms the widespread experience on Kraft linerboard machines that unnecessarily low pH values (pH<5) cause precipitation of pulp-derived lignin, which leads to impaired drainage, so the pH is kept as high as practicable for the chosen sizing regime. For this reason, there has been some interest in this sector in moving away from the traditional rosin sizing to sizing with AKD (see this example of sizing an unbleached Kraft pulp). Unlike the fine paper sector, the use of calcium carbonate is not a factor in such moves, but, on machines using at least some recycled pulp, some calcium carbonate is invariably present and this can cause problems when operating at an acidic pH. There are also issues to do with increasing the paper strength and the consequent ability to use weaker, cheaper fibres at more neutral pH. Alum (or PAC) is still used under neutral pH conditions, but at much lower doses, in order to improve drainage of the stock. Overall, this change can result in increased output, lower chemical costs and better runnability.

On 100% recycled liner machines, the chemistry is more complex due to the high levels of dissolved solids in the recovered paper, which is mainly old corrugated cases. This is discussed further under fluting as the issues are broadly comparable.

Linting

This is a surface characteristic of papers and refers to the loss of fibre fines or fillers from the paper surface during printing. This may also be referred to as dusting. It is caused by poor surface strength and bonding of fine particles. The term "picking" is used for the similar effect of fibre lifting or loss during pressing or paper drying.

Lipophile

A lipophilic substance has an affinity for hydrocarbon substances or can be wetted to some degree by oils and greases. It is relevant to the subjects of interfacial energy and surface tension.

Liquid packagings

This is very specific grade of packaging paper/board that is manufactured to contain liquids, usually beverages of some description. Although the actual paper substrate does not contact the liquid in most cases, it is still important that the papermaking materials meet relevant requirements in terms of food contact and are able to resist the contained liquid. The products used for this application are multi-ply boards that can contain mechanical pulp (usually CTMP) in the middle plys and either an unbleached or bleached chemical (Kraft) pulp for the back and liner plys. As for all packagings, stiffness is a key requirement and hence the use of bulky mechanical pulps in the middles. The body of the paper is sized and, in order to be resistant to the effect of acidic liquids (eg lactic and citric acids), this means that the sizing is normally carried out with alkylketene dimer. The barrier properties of liquid packaging are usually provided by coating with polyethylene alone or with aluminium foil.

Locust bean gum

This natural hydrocolloid gum is a galactomannan polymer obtained from the carob tree. The polymer has a long backbone of β-1,4-linked mannose units with a single pendant α-1,6-linked galactose unit at intervals. The mannose:galactose ratio is about 4:1, but the galactose side units are not distributed uniformly, there being long stretches of mannose units with no galactoses attached (unlike the galactomannans in guar gum). Its molecular mass is 0.3-0.4M Daltons. This gum has been looked at for applications in papermaking (such as a formation aid), but is less widely used than guar gums.

Lubricants

These chemicals are used in coating formulations to reduce their frictional resistance to other surfaces (notably the coating head) during coating application, thus conferring a number of additional benefits such as a smoother coating with less tendency to form streaks. Chemicals used for this purpose are usually low surface tension substances, the most common being:

- stearates either as soluble soaps (eg sodium, ammonium salts) or insoluble salts (eg calcium or aluminium) in emulsion form
- polyethylene in emulsion form
- polyethyleneglycols, the higher molecular weight solids being best for this application
- waxes in emulsion form.

Lumen

This is the hollow centre within wood fibres.

LWC

This is an abbreviation for light-weight coated as in light-weight coated papers.

Magnesium

Magnesium (Mg) is an alkaline earth metal (molecular weight 24) and is a quite common element in papermaking systems, occurring in various forms:

- as the magnesium cation in fresh and machine waters where it may be present most commonly as part of the temporary hardness (as the bicarbonate) or the permanent hardness (as the sulphate)
- adsorbed onto particulate surfaces through electrostatic attraction to surface anionic groups such as carboxyl (see this example of its ion exchange properties)
- combined in minerals such as talc and hectorite.

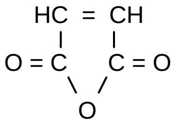
In the dissolved state, it can be analysed for simply by carrying out an EDTA titration at neutral and alkaline (> 11) pH, the difference between these two titrations being due to magnesium which is precipitated as the hydroxide at high pH.

Maize starches

These are also called corn starches and are one of the most common types of starch used in papermaking. They have a lower amylopectin content than potato starches and contain some fatty material (see this table for comparison with other starch types). The fatty content is about 50% free fatty acids (much higher than in wheat starch), which can react with cations such as calcium.

Maleic anhydride

This is the anhydride (without-water form) of the unsaturated dicarboxylic maleic acid (see formula at right). This is used in the manufacture of several papermaking sizes - fortified rosin sizes, ASA sizes and styrene-maleic anhydride sizes.

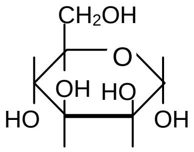


Maltose

This is the disaccharide formed between two α-1,4-linked glucose units, the type of bond present in starches.

Mannose

This is one of the five monosaccharides that are present in hemi-celluloses. It is a hexose with the formula $C_6H_{12}O_6$ and the structure shown here (drawn with a pyranose structure in the α-anomer form - see glucose for explanation of these terms). Mannose is also one of the two monomers in guar gum and locust bean gum and the uronic acid of mannose is one of the two monomer units making up alginates.



Marble

This is one of the several different natural forms of calcium carbonate, the mineral widely used as a wet end filler or paper coating pigment. Marble is a metamorphic form of limestone/chalk, in which the physical characteristics have been changed by heat and pressure. The main characteristic that differentiates marble carbonates from limestone/chalk is their high brightness.

Mass

Although this is a very fundamental parameter, it merits a brief mention as it is so widely used within many papermaking parameters. Mass and weight are often used interchangeably, but they are in fact different entities. The strict definition of mass is that it is the property of a body that causes it to have weight in a gravitational field, ie weight is a result of the action of gravity on a body's mass or weight = mass x gravity. The unit of mass in the SI system is the kilogram (kg), but multiples or sub-multiples of this are probably more commonly used in papermaking, eg tonne (1000 kg) or milligrams (mg = 10^{-3} gram).

Mass features in many papermaking measurements:

- ☐ the grammage of paper products as g/m^2
- ☐ all strength parameters through its contribution to the basic unit of force - the Newton
- ☐ consistency measurements either as the mass % or mass per unit volume (mg/l or g/l)
- ☐ the specific content of component substances, eg kg of X substance per tonne pulp, where the pulp mass is usually expressed on an air-dry (AD) basis or at a nominal 90% dryness.

Mechanical pulps

These pulps account for about 20% of total virgin pulp production. They are characterised by having a reasonable strength (but not as high as for chemical pulps) combined with good light-scattering. They are produced mainly from wood fibres (notably from softwoods) as mechanical treatment would cause excessive damage to the shorter hardwood and non-wood fibres. However, hardwoods such as poplar are used for some grades, but spruce species are usually considered to be the best for production of mechanical pulps. Mechanical pulps are characterised by a high yield, but, as a result of retaining most of the wood lignin, all mechanical pulps have a strong tendency to darken when exposed to light, a phenomenon known as brightness reversion.

This section provides a descriptive overview of the general characteristics of the main types of mechanical pulp with further details of their chemistries being given under each pulp heading. There are three broad categories of mechanical pulp:

- ☐ the basic unbleached grades which are produced by the two main mechanical pulping variants:
  - groundwood processes such as the traditional stone groundwood (SGW) and the more recent pressurised groundwood (PGW) processes
  - refiner-based processes such as the original refiner mechanical pulping (RMP) and the thermomechanical pulping (TMP) processes.
- ☐ the bleached grades where an extra stage is added to any of the basic mechanical processes using two possible bleaching chemicals:
  - hydrogen peroxide, which is an oxidising bleach used under alkaline conditions
  - sodium hydrosulphite, which is a reducing bleach used under slightly acidic conditions
- ☐ chemimechanical pulps, where any of the basic mechanical pulping stages are preceded by chemical impregnation of the raw fibre in order to increase the strength of the resultant pulp.

The process yield from wood is very high for the unbleached pulps (95-97%) and is somewhat lower for the bleached grades (notably those bleached with peroxide), but is reduced substantially (down to as low as 85%) when chemical pre-treatment is employed. All types of mechanical pulping process have the normal auxiliary stages after pulping (see this general diagram), but the emphasis in mechanical pulping is more on screening (and reject treatment) than on washing. Mechanical pulps are always thickened after the pulping stage, but more in the interests of recovering hot water for return to the pulping stage than on removing dissolved solids from the pulp. However, washing is becoming more common, particularly after a bleaching stage, in order to minimise possible problems in the paper machine system from dissolved solids carried forward with the pulp. An example of the change in dissolved organics on bleaching and thickening/washing is shown here for a groundwood pulp.

With the exception of the chemimechanical grades, mechanical pulps are usually produced fully integrated with on-site paper production. As mechanical pulps are the cheapest type of virgin pulp, they are used wherever possible, but their relatively low strength (compared to chemical pulps) and brightness reversion limit their use to certain grades such as short-duration printing papers and certain packaging papers/boards:

- newsprint qualities for newspapers and telephone directories
- SC and LWC papers for short-life magazines and other printing qualities
- folding boxboard mainly for food packaging.

The markets for chemimechanical pulps are different and will be described under that heading.

The key mechanical pulp characteristics are:

- strength in terms of the dry strength of the final product and the wet web strength during water removal (particularly for low grammage products).

  The tensile index of mechanical pulps is 10-50 Nm/g (up to 70 Nm/g for CTMPs) compared to 50-100 Nm/g for bleached Kraft pulps. TMPs are the strongest in terms of both tensile and tear strengths. Mechanical pulps are thus not as strong in the first instance as chemical pulps, but they do retain a higher proportion of their strength on recycling.

- ply-bonding for multi-ply boards

  A high fines content is essential so this favours groundwood over refiner pulps.

- light-scattering and brightness in terms of the functionality of the printed product.

  Light-scattering coefficients of mechanical pulps are 50-80 m^2/kg compared to 20-40 m^2/kg for CTMPs and chemical pulps. Being the strongest mechanical pulp, TMPs have inferior light-scattering to groundwoods.

- freeness in terms of water removal in papermaking.

  All mechanical pulps can be produced to a freeness specification, which is typically 70-120 ml CSF for newsprint and 20-60 ml CSF for SC/LWC papers.

The normal choice today for a new mechanical pulping process is between TMP and PGW, both having pros and cons. TMP has the highest energy consumption, but a lower investment cost than PGW. The greater strength of TMPs means that less reinforcement chemical pulp is needed, which compensates for their lower light-scattering. Overall, TMP is probably most suited to newsprint and boxboard grades and PGW to SC and LWC papers.

From a wet end chemistry viewpoint, the key characteristics of all mechanical pulps are:

- a high content of fine particulate material
- potential for pitch deposition due to the presence of most of the wood's extractive fraction
- potential for dissolution of natural wood substances and those modified by the pulping process.

The fines content of mechanical pulps is greatest for groundwoods (28-45%) with normal TMPs being at the bottom end of this range and CTMPs around 20%. As mechanical pulps are not usually refined before papermaking, the fines present are largely primary fines, ie those generated in pulping. These have a similar composition to the parent wood, ranging from an average wood composition to close to pure lignin for fines from the middle lamella and the S1 layer. Mechanical pulp fines contribute significantly to the quality of wood-containing papers, but the fines must be well-bonded to avoid problems of picking/linting in uncoated grades. However, as well-bonded fines are less effective at light scattering, opacity then declines. Understanding some of the conflicting effects of mechanical pulp fines on paper properties is helped by dividing the fines into two fractions that have been labelled “fibrils” and “flakes”. It appears that the “fibril” fines improve sheet strength, whilst the “flake” fines improve sheet opacity. The surface area of mechanical pulps is 3-8 m^2/g depending on its particle size distribution with values of 1 m^2/g for the P28/R48 fraction and 1.5-2.5 m^2/g for the P48/R100 fraction from a Bauer-McNett classification.

The fines content of mechanical pulps is generally 25-35% (but can be higher), which means that the thin stock may have fines contents of around 50% on virgin pulp-based newsprint machines operating with what are normal, but rather low, fines single pass retentions (see figure at right). With such high fines levels, the total SPR (being a mixture of the fibre and fines SPRs) can easily drop below 60% even when the fines SPR is no lower than 40%.

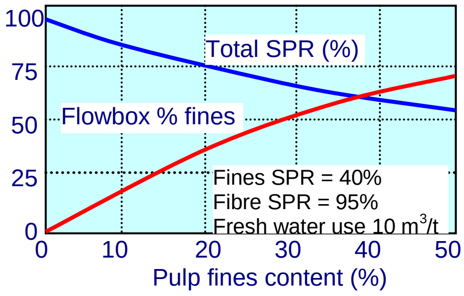


Image analysis has shown that, for several samples of both groundwood and refiner pulps, the longest linear dimension of the fines fraction averages around 25μ with a skewed normal distribution of values from about 10 to 50μ. The fines fraction of mechanical pulps contains some of the extractives responsible for pitch, particularly the small (0.5-1μ) colloidal agglomerates that are the most troublesome. Pitch-forming materials are also present in tracheids and parenchyma cells, both inside the material and on the surface. Although this form of pitch causes fewer problems, pitch can still be deposited when pressure is applied to the fibrous material, eg in the press section.

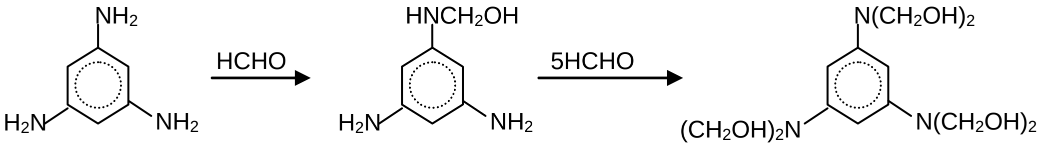
As noted above, most mechanical pulping processes are fully-integrated with paper production, which means that there is a possibility for high carry-over of dissolved solids to the paper machine system unless an efficient final washing stage is installed. This aspect used to be somewhat neglected as the level of dissolution during grinding and refining is very limited. However, the greater use of a final bleaching stage involving hydrogen peroxide (and its inherent increased load of dissolved solids) has led to the wider use of final washers.

One of the factors limiting the dissolution of organics from mechanical pulps (both during pulping and in papermaking) is their low swelling ability, which is restricted by their high lignin content. The water retention value of mechanical pulp is typically around 1g water/g pulp, which is about half of that for chemical pulps. The stiffening effect of the lignin may be partially overcome by increasing the content of anionic groups, eg by the sulphonation that occurs during sulphite pre-treatment or by peroxide bleaching (see this example for pre-treatment with caustic soda). An example of dissolution from mechanical pulps is shown here for a chemithermo-mechanical pulp.

The content of charged organic substances in unbleached mechanical pulps is comparable with the original wood, but it increases on bleaching due to hydrolysis of esters and on chemical pre-treatment due to the introduction of new charged entities (eg sulphonates). Because of the limited swelling of mechanical pulps, the charged substances tend to remain on the fibre with little dissolving as anionic trash. Some charge data for selected wood species is given for birch, pine and spruce under those headings. Data on levels of charged substances in unbleached thermomechanical pulps, bleached mechanical pulps and CTMPs are given under those headings. The variation in the cationic demand on a paper machine using a mixture of unbleached and bleached TMP is shown here. It has been shown that enzymatic treatment of the papermaking pulp with pectinase can reduce its cationic demand.

Melamine-formaldehyde (MF) resins

These wet strength resins are made by reacting melamine (made from urea or dicyandiamide) with formaldehyde to yield a series of methylol derivatives, ultimately hexamethylol melamine (see figure below). There is a wide range in the formaldehyde:melamine ration used in the production of the commercial MF resins, but the most commonly-used derivative is trimethylol melamine (TMM). Under acid conditions (pH 2 with hydrochloric acid), polymerisation of TMM occurs via condensation reactions between methylol groups (to give ether linkages) or between methylol and nitrogen hydrogens (to give methylene linkages) on adjacent melamine derivatives. The acid-catalysed polymerisation is self-limiting at about 20 linked melamine units to form a colloidal dispersion with a visible (blue-coloured) opalescence. This process can be carried out by the chemical supplier or at the mill using an appropriate methylol derivative, in both cases the process taking place at about 6% solids content. Whereas the water-soluble UF resins are retained by adsorption on the particulate matrix, the MF colloid is retained by a hetero-flocculation mechanism, there being some electrostatic attraction to the negatively-charge fibre due to protonation of the nitrogen atoms under acid conditions.



Monomethylol melamine Hexamethylol melamine

Once retained, MF resins need acid conditions to cure, but they are less pH-sensitive than UF resins and can tolerate a sheet (and hence wet end) pH as high as 5.5 (although full cure does then take longer). MF resins do cure more rapidly than UF resins and achieve 60-80% of the ultimate wet strength at the reel, full cure taking no more than about a further 10 days storage. The final polymerisation to confer wet strength is mainly a homo-reaction to create more methylene cross-links between MF units, but there is also some evidence for a hetero-reaction with cellulose hydroxyls. This is consistent with the observation that dry strength improves significantly more (in absolute terms) than does wet strength for MF resins (unlike UF resins).

The superior mass-for-mass wet strength characteristics of MF over UF resins are counter-balanced by greater cost and by the deleterious effect of sulphate ions on performance. However, the latter effect can be ameliorated by using extra formaldehyde during manufacture (so-called high efficiency [HE] resins), which extends the sulphate threshold from about 200 to 1200 mg SO_4/l, but this is at the expense of higher releases of formaldehyde to atmosphere during papermaking. MF resins are best added at the end of the thick stock system just prior to the fan pump and can be dosed as supplied (ie about 6% solids content) when there is good mixing. Otherwise, pre-dilution (with acidified fresh water or clarified whitewater) down to about 1% solids content should improve resin performance. Addition rates vary with the grade and the wet strength specification, but are typically 1-3% resin solids on pulp for products such as banknote paper and label paper.

Like UF resins, the issue of free formaldehyde content in relation to atmospheric emissions is very important. MF resins can contain up to 5% free formaldehyde, but this can be reduced to below 0.5%, albeit with some loss of efficacy. MF resins can also be produced in a nonionic or anionic for use in paper coating, where their function may be to confer wet strength or to act as cross-linking agent for water-soluble binders such as starch. These applications tend to use products with a low free formaldehyde content (<0.5%). Repulping of MF resin-treated broke is somewhat more difficult than UF resin-treated broke, but the repulping conditions are similar, ie acid pH (3-4) at high temperature (60-80°C), albeit for a longer time.

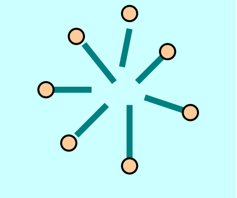
Metamerism

This phenomenon occurs when a paper appears to have a different colour under different illumination conditions, eg daylight against artificial light. It can be a problem when attempting to match colours which appear the same under one illuminant and different under another.

MG

This abbreviation refers to machine-glazed papers made on a machine with a single, large drying cylinder. Adhesion to the cylinder gives one side of the paper a glazed (glossy) finish. Such papers are most widely used for wrapping or bag papers.

Micelle



This is a type of association colloid, which is produced when the concentration of a surfactant solution exceeds a critical level (the critical micelle concentration, CMC). In a micelle, the hydrophobic ends of the molecule are oriented towards one another as shown here and the micelle can be used to solubilise hydrophobic solids. At higher surfactant concentrations, the micelles can form long rods and clusters of hexagonally-packed rods. As a result of micelle formation, the behaviour of surfactant solutions usually shows discontinuities at the CMC, eg the conductivity declines (due to the micelle limiting the mobility of the counter ion associated with the charged hydrophilic end of the surfactant) and turbidity rises (due to light scattering).

Microbiological chemistry

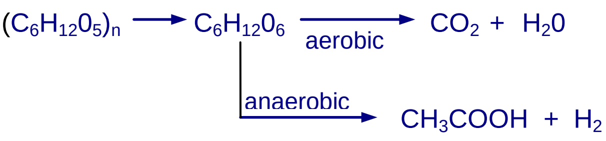
When micro-organisms (bacteria and fungi) grow, they change the chemistry of the substances which they use as a food source. The control of micro-organisms and the various problems they introduce is an important facet of wet end chemistry and of dry end chemistry within size press and coating systems. Some of the commonest food sources in papermaking are polymers (such as cellulose and starch), which have to be broken down initially by extracellular enzymes to smaller molecules such as glucose, which can enter the biological cell, where they are broken down further by intracellular enzymes.

Examples of such chemical transformations are:

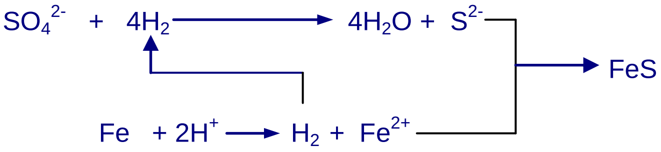
- degradation of fibres by cellulase enzymes to produce shorter, weaker cellulose chains

$$(C_6H_{12}0_5)_n \longrightarrow (C_6H_{12}0_5)_{n-m} + (C_6H_{12}0_5)_m$$

- degradation of starches by amylolytic enzymes which produce water and carbon dioxide under aerobic conditions, but, under anaerobic conditions, a range of organic acids and hydrogen gas



- degradation of sulphate to sulphide by sulphate reducing bacteria, which may use hydrogen from the iron corrosion cell thus expediting the corrosive reaction.



Microbiology

This is the study of micro-organisms, which are generally living forms that are not visible to the naked eye. There is no deliberate harnessing of microbiology in papermaking (see biotechnology), although separated enzymes have begun to be used in recent years for various applications.

Micro-organisms

There is no deliberate use of micro-organisms within the papermaking process itself, but biological treatment systems have been used for a long time to remove BOD from mill wastewaters. There are two types of micro-organism present to varying degrees in most papermaking systems - bacteria and fungi, which get there through their presence in various raw materials (particularly water and pulps). Both sets of micro-organisms create various problems in the papermaking process.

Microbiological problems

Microbiological growth can occur at the wet end of all papermaking systems due to the presence of bacteria and fungi in many raw materials and the suitable growth conditions provided (eg plenty of organic food such as starch and an optimum temperature range of 20-40°C). Microbiological problems are not restricted to the wet end of the paper machine and can also occur within size press and coating systems, where the concentrations of nutrients are inherently much higher.

In addition to the loss of functionality and changed chemistry of raw materials when they are used as a source of energy by micro-organisms, there are various undesirable aspects associated with the generated by-products:

- deposition of slimes in the papermaking system and possibly in the product from growing micro-organisms
- microbial residues in the final paper

- ❑ entrainment of gases, notably of CO_2 leading to possible foam , poor drainage and impaired paper formation quality
- ❑ accelerated corrosion from sulphate reduction and from production of acidic substances
- ❑ safety problems from some product gases, notably hydrogen and hydrogen sulphide
- ❑ generation of odours from organics acids and hydrogen sulphide
- ❑ dissolution of calcium carbonate (when present) from generated acidity, leading to soluble calcium ions and the release of even more carbon dioxide.

These problems can be controlled using the same hierarchy of techniques summarised generally for all problematic substances. In terms of microbiological problems, these are:

- ❑ selecting raw materials with the lowest possible content of micro-organisms and of those substances that are essential to them.

  No papermaking raw material can be guaranteed to be sterile, but most could be pre-treated to achieve this objective. In practice, this is only done for the mill's fresh water through the application of conventional disinfection techniques. A major source of bacteria and fungi is pulp even though purchased lap pulps have been exposed to high temperatures in drying and bleached pulps have also been exposed to biocidal chemicals during actual bleaching. For most micro-organisms in papermaking, biodegradable organics are the most ubiquitous food source, but control of their entry to paper machines is virtually impossible other than by eliminating the use of starches. For other micro-organisms such as sulphate-reducing bacteria, exclusion of sulphate is also difficult due to its common presence in raw waters, but eliminating use of alum and sulphuric acid would still make a positive contribution to controlling this problem.

- ❑ so far as it is practicable, optimising machine operation to minimise the opportunity for micro-organisms to utilise available nutrients.

  The biggest contribution to this can be made by maximising the single pass retention of all starches so that they do not build up in the system. For surface-added starches that are recycled in mill broke and recovered paper, this means minimising dissolution (best done by using cationic starches) and, for wet end starches, this means maximising their adsorption on the particulate matrix (again, in most, but not all, cases best done by using cationic starches of the optimum cationicity). Some form of integrated biological treatment to remove nutrients from machine waters can be particularly helpful on machines with fully or approaching fully closed water systems. In terms of "good housekeeping" practises, regular machine cleaning of not only the wet end system, but also of the starch preparation plant is very important. Of these techniques, only the last one is relevant to microbial problems during surface application.

- ❑ dosing of chemicals to control microbial growth

  There are two possible approaches to chemical treatment:

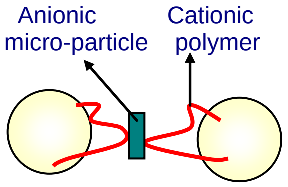
  - the addition of chemicals that kill micro-organisms, ie biocides.

    This has traditionally been the most common technique to deal with micro-organisms in the papermaking system and is still widely used, but alternative techniques are becoming more popular on environmental grounds.
  - addition of chemicals that prevent slime accumulation

    This technique employs a range of mechanisms such as chemical dispersion, enzymatic dispersion and inhibition of biofilm attachment, but has little impact on the microbial populations within machine waters.

Micro-particles

This terminology was first used in the 1980s with the introduction of the Compozil retention/drainage aid system by Eka Chemicals. In this case, the term micro-particle referred to the colloidal silica component of the system, but this is probably better termed a nano-particle system as its dimensions are measured in nanometres (10^{-9} metre) rather than microns (10^{-6} metre). Since then, other chemicals or chemical systems used as retention/drainage aids have utilised this terminology, notably those using bentonite (eg Ciba's Hydrocol system) and, more recently, systems using organic polymers (eg branched polyacrylamides) which act like micro-particles. The driving force behind the development and use of these systems has been the desire to combine good retention and drainage characteristics with better paper formation than is possible by conventional polymer-based systems (see this diagram). Although all of these products have very different chemistries, they all function though a charge-related interaction with a pre-added cationic polymer, as visualised at right.



Middle lamella

This is the thickest, outermost layer within wood fibres and comprises close to 100% lignin.

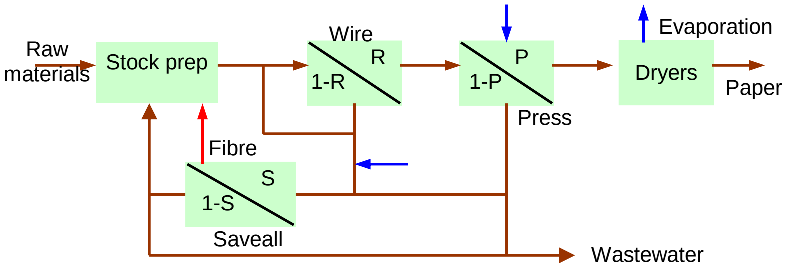
Minerals

These are defined as non-living chemical compounds that occur naturally in the earth and is usually applied to inorganic compounds, but it is also used to describe materials such as mineral (natural) oils. In papermaking, the main minerals used are those used as fillers and pigments such as calcium carbonates and clays.

Modelling

Wet end chemistry is concerned with the numerous interactions between components of the wet end furnish, the outcome of which affect their single pass retentions and hence their concentrations for a defined water balance. A simple steady state model of the papermaking system is very helpful to look at the inter-relationships between retentions, the degree of fresh water use and circuit concentrations.

The model is based on the paper machine circuit shown here, but is best re-drawn in a more schematic form (as at right) to understand the various inputs/ outputs and fractionations. The input variables can be selected to simulate the conditions on any paper machine. No cleaning stages are included so there is no deliberate removal of materials. Consequently, the only loss of materials is via the normal machine wastewater due to the single pass retention and saveall recovery of all materials being less than 100%. Fresh water consumed on ancillary circuits such as vacuum pump sealing, cooling and hoses does not have to be considered as we are only interested in the main papermaking circuit.



The specified input variables are:

- ❑ fresh water used within the main papermaking circuit and in the press section
- ❑ mass of pulp input and its contents of fines and dissolved solids
- ❑ filler content of the product
- ❑ single pass retentions of pulp fibre, fines and filler
- ❑ flows of thick stock, thin stock, couched sheet, pressed sheet and recycled press section water
- ❑ saveall recovery efficiency for fibre, fines and filler
- ❑ energy dissipated or deliberately added to the wet end (needed solely to calculate temperatures)
- ❑ additive distribution between liquid phase (non-adsorbed) and adsorbed on fines/fibre fractions.

The calculated output variables are:

- ❑ total retentions and losses of all specified components
- ❑ paper production and composition
- ❑ single pass retentions of mixed components, eg fibre + fines
- ❑ masses, concentrations and temperatures at all locations around water circuit.

The model is used for illustrative purposes at several places in this text to show:

- ❑ the dependence of total retention on single pass retentions shown here
- ❑ the dependence of circuit concentrations on single pass retentions shown here
- ❑ the dependence of total retention on degree of water closure shown here
- ❑ the dependence of circuit concentrations and temperature on degree of water closure shown here
- ❑ the dependence of the total and single pass retentions of an additive on its adsorption shown here
- ❑ the dependence of the retentions of an additive on the degree of water closure shown here.

Molarity

This is the concentration of a chemical species expressed in moles (gram molecular mass) per litre of solution and is usually abbreviated as M, ie a solution containing 400 mg calcium/l has a molarity of 0.01M.

Mole

This is the molecular mass of a chemical entity expressed in grams and is used in the molar concentration scale.

Molecular mass/weight

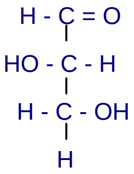
This is the mass of any substance determined by adding up the mass of all the atoms in the substance's molecular formula, the units being Daltons (Da). For example, the molecular mass of calcium carbonate is 100 Da and of each anhydroglucose unit in the starch or cellulose chains is 162 Da. For substances of uncertain molecular mass (eg polymers), it can be estimated from measurements of its intrinsic viscosity. One mole of any substance contains exactly the same number of molecules - this is Avagadro's number, which is 6.023×10^{23} molecules/mole.

Monodisperse

This is a term used in colloid chemistry to denote particles having a very narrow range of particle sizes, in contrast to polydisperse particles like all papermaking raw materials. It is also sometimes used in an analogous way in relation to the molecular weight range of polymers, ie polymers with a very narrow range of molecular masses.

Monosaccharide

This is a type of carbohydrate that cannot be broken down into a simpler compound as it contains only one saccharide unit. One of the simplest monosaccharides is glyceraldehyde, which is not itself relevant to paper chemistry, but is important as it forms the basis for discussing the configuration and conformation of sugar molecules. As is evident from the its formula (shown at right), glyceraldehyde contains one asymmetric carbon atom at its centre and so exists in two different forms (enantiomers, related to isomers), which are able to rotate the plane of polarisation of plane-polarised light to the same extent but in opposite directions. These two forms are labelled dextrorotatory (D) and laevorotatory (L) and are arbitrarily written with a certain structure. The form of glyceraldehyde shown here is the L form, whereas the D form has the central H and OH groups reversed. Other monosaccharides are labelled D or L depending on which form of glyceraldehyde they can be formed from or broken down to. These stereochemical aspects of the monosaccharides are not of great importance to paper chemistry. There are two important classes of monosaccharide in some papermaking raw materials - the pentoses and the hexoses.



$$\begin{array}{c} H - C = O \\ | \\ HO - C - H \\ | \\ H - C - OH \\ | \\ H \end{array}$$

Montmorillinite

This mineral is the main constituent of bentonite clays and is described further under that heading.

Mottle

This term is applied to the finished paper when it has a blotchy, non-uniform appearance and is an example of non-uniformity in the x-y plane of the paper. It is most commonly used in relation to printing paper where the printed image has a blotchy appearance. It can be caused by variabilities in the printing ink(s), the printing process and also in the paper itself due to surface inhomogeneity and consequent variability in ink receptivity. Some papers (eg white-top liners) have a deliberately mottled appearance.

Nano-particles

Nano-particles are particles with dimensions measured in several or maybe tens of nm (10^{-9} or one billionth of a metre). So-called nano-technology is becoming an important industrial category, but nano-particles have been used in papermaking for some time, although they were originally termed micro-particles. The best example of such technology is colloidal silica.

Natural papermaking

This term is not widely used and is therefore not well defined, but it raises interesting questions about the optimum state of the papermaking process in relation to the papermaking pH. Natural papermaking could be defined as operating at the pH dictated by the pulp and any filler used in the mill's normal fresh water supply. In most cases, this pH would be consistent with neutral papermaking.

Neutral papermaking

Although there is no universally-accepted definition, neutral papermaking can be defined as where the wet end pH is in the range 6-8. This is the most common type of papermaking today due to the availability of additives that function well over this pH range. The potential benefits from neutral papermaking are usually judged in relation to an existing paper machine running under acid conditions as this is the normal alternative. There are many potential benefits to operating in this neutral pH range:

- ❑ operating at what is the natural pH of the system, thus obviating the need for addition of acid or alkali or for strict pH regulation and control
- ❑ facilitates the use of calcium carbonate as a wet end filler or coating pigment
- ❑ stronger fibres due to increased swelling ability
- ❑ stable charge chemistry on pulps as the charge-determining carboxylic acid groups are fully ionised and thus present as carboxylate anions
- ❑ any use of alum or PAC is in the pH region where their charge chemistry is more stable
- ❑ less corrosion of wet end equipment and consequent ability to use cheaper, less corrosion-resistant materials of construction
- ❑ improved permanence of the paper due to reduced strength loss on prolonged storage.

Some of the changes (such as the impact on the overall charge balance at the wet end) are complex and multi-faceted. The increased anionicity might be interpreted, at first glance, to be disadvantageous as it increases the repulsive charge between particles, but it also allows a stronger interaction between particle surfaces and cationic additives, which is beneficial in relation to aggregation of fines and adsorption of functional additives. An adverse consequence of the increased anionicity would be the increased charge on anionic trash and the increased fibre swelling can lead to greater dissolution of such substances in the first place. A neutral pH also happens to be region where micro-organisms grow most rapidly and this certainly does put pressure on achieving adequate microbial control.

Neutral sulphite semi-chemical (NSSC) pulps

These virgin pulps are used virtually exclusively in the manufacture of fluting or corrugating medium. The most common raw materials are mixed hardwoods, but pulps suitable for fluting medium are also made from non-wood fibres such as straw. In the latter case, a simpler soda pulping process is commonly used and this is also sometimes the case for hardwoods. The cooking conditions in NSSC pulping are much milder than in full sulphite pulping so the yield is maintained at, what is for a chemical pulp, a high level (80-85%). The cooking chemicals are sodium sulphite (10-20% on wood) and a low dose of sodium carbonate or hydroxide to provide an alkaline buffer against the organic acids released on heating the wood.

During cooking, the content of charged groups increases due to sulphonation of lignin's phenylpropane units and hydrolysis of carboxyl esters. Although such pulps are always washed after mechanical treatment, removal of the lignosulphonates is not easy and paper machines using these pulps have to contend with significant levels of anionic trash in the form of lignosulphonate. Fortunately, the main paper grade using NSSC pulp (fluting medium) requires few wet end chemicals, but it is difficult for conventional retention or drainage aids to function in the presence of high lignosulphonate levels (see examples here for polyethyleneimine and here for polyacrylamide).

Neutron

This is the uncharged mass in the nucleus of the atom. Its mass is the same as that of the proton.

Newsprint

This is one of the main grades of graphical paper within the wood-containing sector. Newsprint is made from a variety of furnishes from 100% virgin pulp to 100% deinked pulp. For virgin pulp newsprint, the maximum quantity of mechanical pulp (80-100%) and the minimum content of bleached chemical (reinforcement) pulp (0-20%) is used to give the required balance of strength, brightness and opacity. For deinked newsprint, the standard furnish for deinking is an approximate 70:30 mixture of old newspapers and old magazines to give the optimum balance of pulp types. Newsprint may also be made from a mixture of deinked and virgin (usually just mechanical) pulps. In either case, the newsprint mill would normally be fully integrated with on-site mechanical pulping and/or deinking, any chemical pulp probably being brought-in from outside.

Newsprint is usually made to a particular brightness specification, which dictates the extent of bleaching after pulping or deinking. Standard newsprint has a brightness of 58% ISO, but it is made at qualities up to about 70% or even higher where required. The grammage of newsprint and related grades (eg directory papers) is progressively lowering and now covers the range 36-49 g/m^2 with the median being around 45 g/m^2. Standard newsprint requires no functional chemical additives in the paper, but the following are used on some grades:

- ❑ dyes for colour balancing or coloration
- ❑ wet end sizing (eg with AKD) for water-resistance in printing
- ❑ additives to control paper surface characteristics such as release during pressing and linting, which may be added by surface application rather than at the wet end
- ❑ filler (eg calcined clay) for enhancement of opacity, brightness and surface properties.

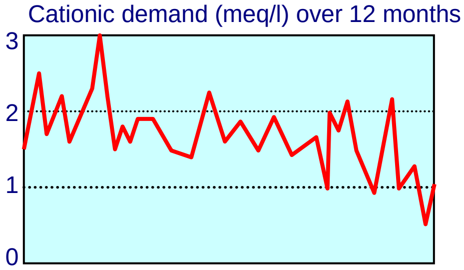
The wet end chemistry of newsprint machines is challenging because of the relatively low grammages and the fast machine speeds (both of which put pressure on the aggregation of the particulate matrix in terms of achieving good single pass retention) combined with the stringent product requirement in terms of formation quality. Most newsprint mills operate with a fresh water consumption no more than about 15 m^3/tonne, which means that the fresh water entering the main papermaking circuit is well below 10 m^3/tonne. This gives a somewhat high concentration factor applied to the load of dissolved substances that, after the thickening stages at the end of the deinking or pulping lines, finally reaches the paper machine system. Combined with the high temperatures in pulping and deinking, the fairly closed water system also means that process temperatures are invariably quite high (around 50^{o}C).

In addition, the pulp furnish represents a potentially difficult set of characteristics in terms of:

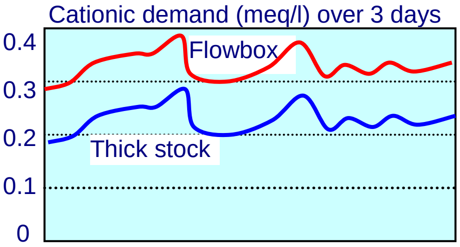
- high fines content from both virgin mechanical and deinked pulps with some recycled fillers (typically 6-8%) always present within deinked pulps
- moderate-high loads of dissolved substances, largely organics (including anionic trash), plus contributions from any added electrolytes (eg acids for pH control)
- depositing substances in the form of pitch from mechanical pulps and stickies from deinked pulps.

Despite the challenging combination of furnish, machine and grade characteristics, the fact that newsprint mills are invariably integrated with pulp production does mean that the quality of the pulp passing forward to the paper machine is under the control of the mill. It is becoming common practice to treat the pulp, at least partially, at the end of the pulping/deinking operation (eg to neutralise anionic trash) rather than entirely on the paper machine.

An example of the variability in one sub-component of the dissolved organics (anionic trash) is shown at right for a newsprint machine using a blend of unbleached and peroxide-bleached TMP. The short-term variability is attributed to the variable proportions of unbleached pulp, bleached pulp and broke, but the longer-term decline in cationic demand is due to a seasonal drop in the need for bleached pulp. The substitution of mechanical pulp by deinked pulp usually means that the level of anionic trash on the paper machine is reduced, in one case quoted by about 10% in increasing the deinked pulp from 10% to 35% of the furnish.



Source: Desharnais et al in Pulp Paper Canada, 2002, 103, 4, 44-46.



Source: Gill, R at COST E14 Workshop “Towards zero liquid effluent in papermaking” , Lisbon, 2000.

The interpretation of published data from paper machines can be difficult because of the often-unstated degree of water recycling, which tends to concentrate the poorly-retained furnish components, ie the dissolved substances. Some typical levels of anionic trash on a 100% deinked newsprint machine are shown at left. The correlation between the two locations is excellent, but the higher concentration at the flowbox reflects the recycling of dissolved solids in the primary loop plus addition of charge-neutralising chemicals.

Another example of the impact of broke on cationic demand is shown here for a 100% deinked newsprint machine. In this case, the cationic demand is clearly reduced when the proportion of broke is increased. The reason for this is that, as newsprint broke contains no surface-applied chemicals, it represents simply a cleaner version of the deinked stock due to the washing effect of papermaking. The effect of residual silicate in a deinked pulp is shown here in terms of single pass retentions.

The level of anionic trash is one of the key factors in selection of retention aids, which are essential on newsprint machines because of the high fines contents, but is constrained by the required formation quality of the product. Because of this, single pass retentions are invariably no higher than 55-60% for the total furnish and 30-40% for the fines. Retention aid systems are always at least two component, common combinations being a highly cationic polymer plus polyacrylamide, bentonite plus polyacrylamide and those based on polyethyleneoxide.

Newton

This is the basic measurement unit for force and is usually abbreviated N where 1N = 1 kg.m/second^2, ie it is the force required to give a mass of I kg an acceleration of 1 m/second^2. The terms "Newtonian" and "non-Newtonian" is also used in rheology to differentiate between fluids with different relationships between viscosity (or shear stress) and shear rate.

Nitrate

This simple anion (NO_3^-) may be present in the papermaking system through its presence in fresh water, but it is not contained in any commonly-used paper chemicals. When it is present, this is quite useful as it can be utilised by facultative aerobic bacteria and thus delay the onset of undesirable anaerobic conditions. One recent chemical used in this form is aluminium nitrate.

Nitrogen

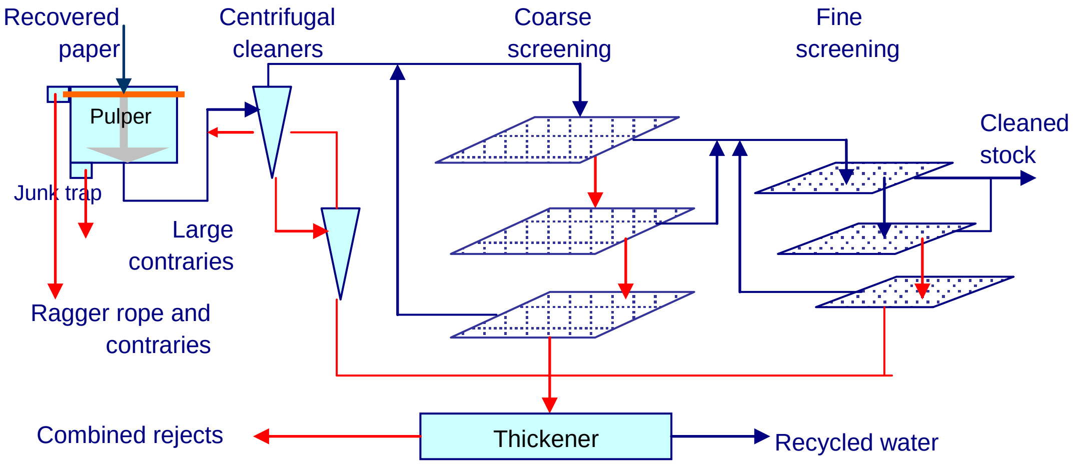
Nitrogen is the lead element in Group 15 of the Periodic Table and is a diatomic gas (N_2). It is present as a dissolved and entrained gas in machine waters simply due to its presence in air and may also be present in simple salts such as nitrate. However, it is most commonly present in papermaking raw materials as an organo-nitrogen compound, where the nitrogen gives the molecule its cationic character.

NMR

This is an abbreviation for nuclear magnetic resonance spectroscopy, an analytical technique used to characterise substances containing certain atoms, notably hydrogen and carbon (as ^{13}C). It has been used in papermaking in attempts to understand the mechanism of AKD sizing.

Non-deinked recycled pulps

This is one of the two broad categories of recycled pulp produced from recovered paper, the other being deinked pulp. All paper machines use a type of non-deinked recycled pulp in the form of their own broke, but, unlike purchased recovered paper, this has the benefit of being of known chemical composition. Recovered paper that enters the papermaking system directly in this way (ie without any deinking) is normally cleaned using a range of mechanical processes, a typical sequence for packaging mills being as shown below.



The losses as rejects in the form of plastics, metals and attached fibre are about 50 kg/tonne recovered paper, but this is increasing due to the ongoing deterioration in the quality of recovered paper. The overall yield from recovered paper in a non-deinking system is typically 90-95% depending on the content of dissolved substances and the degree of water closure, which affects the total retention of particulate and dissolved substances.

Pre-consumer recovered papers are used in many grades with minimal pre-treatment, but the quantities available are usually quite limited. This type of recovered paper is normally used in a very similar grade to the original as this maximises the value and recycle potential (recyclability) of all the components. Non-deinked post-consumer recovered papers are used in several paper grades, notably:

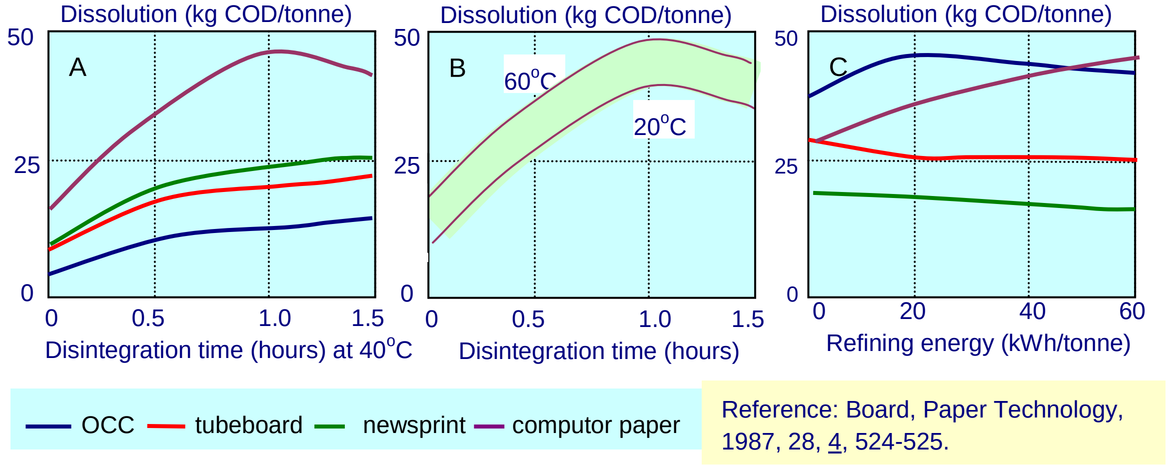
- to make the liner component in corrugated cases, this recycled version of Kraft linerboard being known as test liner
- the fluting medium in corrugated cases
- other packaging grades
- industrial towels.

Both deinked and non-deinked pulps have to cope with the common problem of the fibres having different sets of properties (usually inferior) compared to their corresponding virgin pulps. Compared to deinked pulps, non-deinked recycled pulps are different in two main ways:

- the presence of higher levels of water-soluble substances in the pulp reaching the paper machine. This is a direct consequence of the fact that the stock preparation system is not usually separated hydraulically from the papermaking circuits, so all the material dissolved from the recovered paper passes forward to the paper machine (although this is preventable - see here). The most significant dissolved fraction is the organics due to the high starch content (typically around 50 kg COD/tonne) of the paper grades recovered for use in papers made from non-deinked pulp. In addition, the water systems of paper machines using such pulps are often highly closed leading to very high circuit concentrations (up to 30-40 g/l as COD). The effect of closing up on circuit concentrations is shown in this example, but note that the assumed level of dissolved solids (2% of pulp) is much lower than from many recycled pulps, ie the dissolved solids would rise to 12-13 g/l when the dissolved solids input is 50 kg/tonne.

- the presence of higher levels of stickies contaminants in the pulp reaching the paper machine. This is a consequence of the higher content of stickie materials in recovered paper grades used as non-deinked pulps (eg old corrugated cases) and their inferior removal in stock preparation compared to deinking.

The dissolution of substances from recovered paper in a non-deinking system depends on process conditions in terms of pH, temperature and electrolyte content, which affect the pulp's swelling ability. As shown in the figure below, the effects of pulp disintegration period and refining period may be different as the latter increases the surface area for re-adsorption and the net dissolution may therefore decrease. By contrast, disintegration simply allows longer contact, but with no significant change in surface area. Increased temperature enhances dissolution, particularly at short disintegration times. For three of the four pulps in the figure below (newsprint being the exception), starch was the dominant substance dissolved on disintegration and refining. The type of starch present in these pulps would have been in-mill converted native starch, which is retained with the pulp only to the extent of 10-30%.



Reference: Board, Paper Technology, 1987, 28, 4, 524-525.

An important sub-fraction of the dissolved organics is anionic trash. Many of the water-soluble, non-fibrous additives in papermaking have some charge character and will thus influence the charge status of the recycled pulp. Published charge data for non-deinked recycled pulps is not plentiful and is often poorly characterised. Quoted values for dissolved charges from corrugated case materials are 2-5 μeq/g, much lower than the charges of the unbleached chemical pulps used to make the original papers. This is in line with expectations as the original charged materials would have been poorly retained (unless the paper was made on a machine with a highly-closed water system) and no highly-charged materials are added during the first making. Other data shown under deinked pulps indicates the level of charged substances from disintegration of wood-free copier papers to be 2-5 μeq/g, of old newspapers to be 2-3 μeq/g and of old magazines 6-9 μeq/g. Addition of caustic soda increased dissolution of charged substances by factors of 2-4 depending on paper type.

Non-fibrous raw materials

Papermaking raw materials can conveniently be divided into fibrous and non-fibrous raw materials. The latter can be added either at the wet end or to the surface of the paper through spraying, impregnation at the size press or by coating. Non-fibrous chemical additives can be broken down into two large groups:

- ☐ product performance additives used to manage some functional characteristic of the paper, the main ones being:
  - minerals for improved opacity and surface smoothness, which are added either as fillers at the wet end or as pigments in coating. This is by far the largest type of additive in tonnage terms.
  - sizes for water resistance, added mainly at the wet end but also at the size press
  - dry strength additives to enhance the strength of paper when dry, which are added at the wet end, at the size press and in coating as a coating binder
  - wet strength resins to enhance the strength of paper when wet, which are added mainly (except for a few speciality grades) at the wet end
  - colorants to add colour, which are added mainly at the wet end
  - fluorescent brighteners for improved brightness, which are added at the wet end and paper surface.

- process control chemicals used to manage some aspect of the process, but which can also indirectly influence product quality. They are mainly added at the wet end, the main ones being:
  - retention aids to enhance the single pass retention of particulate materials, notably the fines fraction, but which also influence a number of other important papermaking variables such as the formation quality of the paper
  - drainage aids to enhance water removal on the papermaking wire
  - chemicals to control chemical deposits such as pitch, stickies, etc
  - chemicals to control process microbiology, which are sometimes added to or incorporated in some functional additives
  - chemicals to control foam (anti-foams or defoamers), which are also added to coating mixes
  - chemicals to control system charge or anionic trash, which are often considered to be part of retention aid systems.

Nonionic

This refers to the lack of charge carried by a substance, the most common references in papermaking being to nonionic polymer and nonionic surfactant.

Non-wood pulps

Non-wood pulps account for around 8% of global virgin pulp production or around 15M tonne in 2000. Production and use of non-wood pulp is concentrated in certain countries with China accounting for 75-80% of this total (ie about 12M tonne in 2000). Non-wood pulps are best classified in terms of their location/function in the growing plant as follows:

- bast (inner layer below bark) fibres such as flax, hemp and jute
- other stem fibres such as bagasse, bamboo and straw
- leaf fibres such as esparto, manilla and sisal
- seed hairs such as cotton.

Non-wood pulps derived from agricultural by-products account for most of the production tonnage (about 75%), the biggest single type being straw pulp which alone accounts for about half of the non-wood total. The approximate order of other non-wood pulps is bagasse (about 14% of total), natural plants such as bamboo (18% of total, mainly in India) followed by industrial crops spread amongst the types listed above. Most non-wood pulps are produced by chemical pulping processes, the exception being bamboo which is also pulped mechanically. Non-wood pulps are used in most papermaking grades in those countries where they are the dominant pulp type, but, in countries based predominantly on wood pulps, they are used for speciality grades such as tea-bag papers (manilla), banknote papers (cotton) and cigarette tissue (flax).

The dominant straw and bagasse non-wood pulps have fibre characteristics comparable with hardwood pulps with fibre lengths of 1-2 mm and diameters of 10-20 microns. However, the more speciality non-wood pulps are characterised by much higher fibre lengths (30 mm for flax and cotton), which, with fibre diameters of 20-25 microns, gives them very high aspect ratios. The relative dimensions of the fibre wall and lumen may be different from those for wood, eg cotton has a rather thin fibre wall and wide lumen whereas the converse is true for flax. Straw fibres have a reputation for poor drainage due to the presence of thin-walled cells. The chemistry of some non-wood pulps is close to that of wood pulps. Straw and bagasse have a carbohydrate:lignin balance similar to that of hardwoods, but straw tends to have a significant mineral content unless well washed prior to pulping.

Flax has a higher cellulose content than wood pulps (about 60%), but the "purest" non-wood fibre is cotton with 80-90% cellulose and less than 5% lignin.

NSSC

This is an abbreviation for neutral sulphite semi-chemical pulps.

Nucleophilic

This term applies to elements or groups that have a strong tendency to repel or donate electrons. Nucleophilic elements (such as sodium) tend to be located at the left-hand side of the Periodic Table. The nucleophilic character of some chemical groups (eg hydroxyl, amino) gives rise to an uneven distribution of electrons within some organic chemicals, which is particularly important for some of their reactions and for the functional properties of certain organic substances, eg dyes and fluorescent brighteners. The opposite type of element or group is termed electrophilic.

OBA

This is an abbreviation for optical brightening agents.

Odours

This may be a surprising topic to include within paper chemistry, but odours are unfortunately a not uncommon occurrence at paper mills. Odorous compounds are not usually present within raw materials (although they may have been at the pulp mill), but can be generated within the process through microbiological activity. There are two main types of odorous substance that can occur in papermaking systems - organic acids and hydrogen sulphide, both caused by microbiological activity under anaerobic conditions.

Olation

In contrast to oxolation, this is the use of hydroxyl groups to form bridges in a polymer chain as might take place with polymerisation of aluminium ions from added alum.

Oligosaccharide

These are carbohydrates containing 2-4 monosaccharides, such as maltose and cellobiose, each having two glucose units joined slightly differently.

On-line monitoring

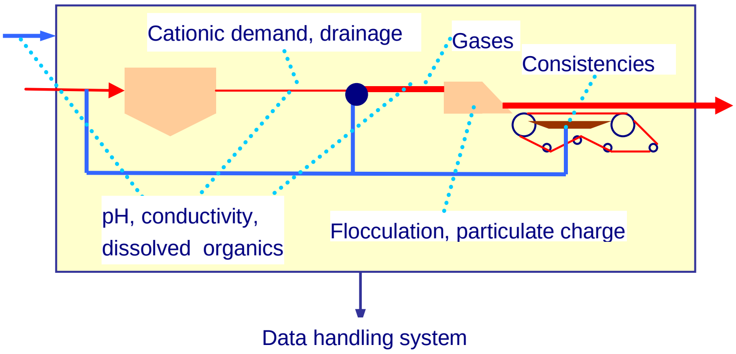
There has always been an incentive to characterise a paper machine's chemical status, but this used to be done exclusively by manual sampling followed by off-line analysis in the laboratory. This is still the technique used by many mills, but others have turned to the use of on-line sensors to measure some aspect of wet end chemistry. This began in earnest during the 1980s, many years after on-line sensors had begun to be used at the dry end to measure paper properties. Until this time, the absence of suitable, proven sensors and the lack of perception of the potential benefits judged against what seemed to be high installation costs were a major constraint on the use of such systems.

On the other side, however, there were (and still are) a number of challenging factors causing mills to welcome the opportunities presented by on-line instrumentation:

- the increasing complexity of wet end chemistry due to:
  - more additives being used both at the wet end and for surface application
  - new virgin pulps being developed, in some cases with greater levels of problematic substances
  - more recovered paper of declining quality being recycled
  - greater environmental pressures on the degree water closure leading to higher process concentrations and temperatures.
- the pressure from faster machines on single pass retentions and the potential to make even more broke if the correct wet end balance isn't achieved
- quality pressures in the market place driven by the interest in documented quality management practises such as the ISO 9000 series
- increasingly limited mill resources to undertake manual chemical surveys and trouble-shooting.

Most sensors are initially installed simply to monitor the variability of a particular parameter. In some cases, it may be possible to control that parameter through chemical dosing, eg retention aid in the case of single pass retentions, cationic polymer for cationic demand, etc. Putting this aspect of machine operation under the control of the sensor takes considerable confidence in its reliability and reproducibility, but is often the medium-term objective behind installing the sensor in the first place. The over-riding focus of on-line monitoring is on stabilising wet end chemistry (eg achieving a more uniform fines single pass retention) rather than on enhancing some particular aspect of wet end operation (eg increasing the fines single pass retention).

The initial focus of research to develop on-line chemistry sensors was on the measurement of particulate consistencies, but this has now extended to cover a range of additional parameters, as summarised in the figure at right:



- ionic chemistry (pH, conductivity, specific ions)

  There are a number of simple sensors from individual suppliers that can be incorporated within a monitoring system. A multi-sensor system was developed by the chemical supplier Raisio during the 1990s and this was later acquired by ABB. This is the WIC system, which can measure a number of chemical parameters - calcium, total and free aluminium, chemical oxygen demand, dissolved organic carbon, silicate, starch and total alkalinity. It can also incorporate sensors for cationic demand and turbidity.

- particulate consistencies, particulate composition, single pass retentions, state of aggregation (flocculation) and turbidity

  These parameters are brought together under one side-heading as they can all be measured with the same sensor unit. Although these sensors have now been commercially available for nearly 20 years, they are still at the heart of any on-line control strategy in view of the central importance of single pass retention, notably of the fines fraction, to wet end chemistry. In the early years, they were used solely in a monitoring mode, but they are now widely used for control of retention aid addition, chiefly via the whitewater consistency value (rather than the calculated SPR).

  The principle of measurement has also evolved over this timescale from simple measurement of the transmitted light from one light source (ie turbid) to the measurement of the angular distribution of the scattered light from one or several light sources. Generally, it is this wider range of output values that has allowed the measurement of particulate components such as filler and of particle (floc) size distribution. Assessment of the state of flocculation utilises the variance, not the absolute value, of the output signal, the variance being greater as the floc size increases. Suppliers for this set of consistency-related parameters include BTG, Cerlic, Chemtronics (Eka) and Metso Automation.

- cationic demand

  There was a strong interest in measuring this parameter on-line for many years before suitable on-line sensors became commercially available during the second half of the 1990s. In nearly all cases, the sensors are based on polymer titration using a streaming current detector for the end-point determination, the one exception being the colloid titration system used within ABB's WIC unit. The most common application has been on coated machines for control of the anionic trash originating from coated broke (see this figure).

- particulate charge (zeta potential)

  The only on-line technique suitable for this parameter is streaming potential of which there a number of commercial instruments, but none have been applied as extensively as SCDs for cationic demand measurement. The precise reason for this is not clear as both measurements should be valuable, SCD more in terms of wet end chemistry and streaming potential more for product quality.

- entrained gases

  This parameter may be measured on-line using at least two quite different principles - the well-known compressibility technique (as in the BTG Mutek unit) and the ultrasonic method (as in the Sonica unit).

- pulp freeness or stock drainage

  These two parameters are affected by many papermaking variables, the freeness parameter usually being judged on the pulp alone whereas drainage may be measured on the total papermaking stock, including any fillers and chemicals. For some furnishes, wire drainage may be more important than wire retention so the drainage value could be used to regulate the dosing of drainage aids rather than of retention aids. There are at least two on-line freeness sensors available (from BTG and Innomatic), which are applied to thick stock for refiner control and at least one on-line drainage sensor (from BTG), which is applicable to the thin stock.

Opacity

Opacity is an important optical characteristic for graphical paper grades in relation to the absence of show-through of the applied image on the reverse side of the paper. There are two common measures of paper opacity:

$$\text{ISO opacity} = \frac{\text{diffuse reflectance of single sheet on very black background } (R_0)}{\text{diffuse reflectance of infinite pile of sheets } (R_\infty)}$$

$$\text{Tappi opacity} = \frac{\text{diffuse reflectance of single sheet on very black background } (R_0)}{\text{diffuse reflectance of single sheet on very white background } (R_\infty)}$$

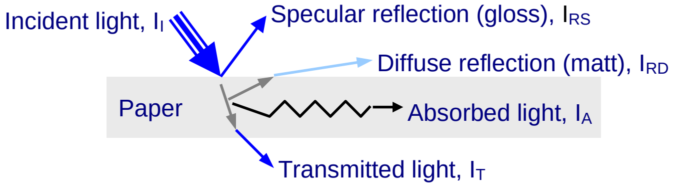
The ISO opacity is sometimes referred to as the printing opacity and is the more relevant to most practical circumstances. In both cases, the opacity is usually expressed as a percentage rather than as a fraction. Opacity is influenced by the paper’s light scattering and light absorption coefficients.

The opacity of paper is affected by many variables, notably the type of pulp used and the type and amount of filler in the paper. Although Individual fibres are quite transparent, the mat of inter-connected fibres is opaque. Maximum opacity is achieved by maximising the number of air-fibre interfaces so pulp refining decreases opacity as the generated fines increase inter-fibre bonding and thus reduce the number of fibre-air interfaces remaining for light scattering. When the paper is saturated with water or oil, the opacity of the paper is reduced due to the lower refraction of light at a liquid/fibre interface than at an air/fibre interface. Mineral fillers improve opacity through a combination of high refractive index and high surface area.

Optical brightener

This is an alternative name for a fluorescent brightener.

Optical properties of paper



$$I_I = I_{RD} + I_{RS} + I_A + I_T$$

$$\text{Reflectance (R)} = \frac{\text{total reflected light}}{\text{total incident light}} = \frac{I_{RD} + I_{RS}}{I_I}$$

As shown at right, light can be reflected directly at an interface or after various internal reflections, both contributing to the sheet's opacity. The spectral characteristics of the absorbed light dictate the spectral characteristics of the reflected and transmitted light and hence the colour of the paper. The most widely-used theory to model the behaviour of light when it meets a hard surface was developed by Kubelka and Munk for paint films, but it is also applicable to paper. This theory separates the effects due to light scattering, which increases both sheet opacity and sheet brightness from those due to light absorption, which increases opacity but decreases brightness. Paper brightness and whiteness are also influenced by the inherent characteristics of the fibres and other materials present.

Organic acids

This covers a wide range of organic substances, but only two types of organic acid are found in papermaking systems:

- fatty acids of both the short-chain volatile and long-chain (non-volatile) types
- lactic acid, which, like the volatile fatty acids, is generated microbiologically .

Organic chemistry

This is one of the three main branches of chemistry and is a vast subject in its own right. It is defined as the chemistry of carbon compounds, excluding carbon itself, its oxides and metal carbonates. The term was originally applied just to the chemistry of compounds produced by living organisms, but it now embraces the huge field of synthetic carbon compounds. There are an enormous number of organic chemicals used in papermaking, but it is useful here to list briefly the different types of organic compound, which are then described further under that heading:

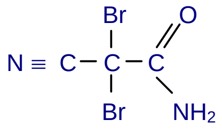
- alcohols, which are organic compounds containing a hydroxyl group
- aldehydes, which are compounds containing the H - C = O group
- amides, which are compounds containing the -$CONH_2$
- amines, which are compounds containing the -NH_2 group
- amino acids, which contain carboxyl and amine groups
- azo compounds, which contain the - N = N - group
- carbohydrates, which are compounds where the formula can be written $C_x(H_2O)_y$
- carboxylic acids, which are organic acids containing the -COOH group and include the fatty acids
- cyanate compounds, which include iso-cyanates and thiocyanates
- dioxins, which are derivatives of the 6 member carbon ring containing two oxygen atoms
- esters, which are compounds containing the O = C - O - C bond
- ethers, which are compounds containing the C - O - C bond

- furans, which are derivatives of the 5 member carbon ring containing one oxygen atom
- hydrocarbons, the simplest type of organic compound, which contain only carbon and hydrogen
- ketones, which are compounds containing the carbonyl C = O group linked to two carbon atoms
- lactones, which are often called internal or cyclic esters
- lignans, which are linked phenylpropane units
- organo-halogen compounds, which are fluorine, chlorine and bromine derivatives.
- organo-nitrogen compounds, which include some very important cationic additives
- organo-phosphorous compounds, which have a few specialised applications
- organo-silicon compounds, which also have only a few specialised applications
- organo-sulphur compounds, which are very important to brightening and colouring additives.
- terpenoids (terpenes), which are hydrocarbons based on isoprene units.

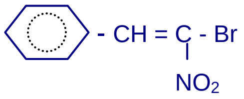
The bonds between atoms in most organic compounds are covalent, but many of the functional groups contain charged entities (eg carboxyl groups) which play a very important role in papermaking. Some organic compounds with the same molecular formula can have different chemical structures and these are referred to as isomers, of which there are several types. Many of the organic compounds used in papermaking are in the form of long-chain polymers and, in fact, there are relatively few non-polymeric organics in use, dyes and fluorescent brighteners being the most common examples in this last category.

Organo-bromine compounds

Organo-bromine compounds are used as biocides, two examples being shown below. DBNPA is available in solid and liquid forms, the latter having some oxidising properties as it contains hypobromous acid. It degrades quite quickly to ammonia and bromide ions. Another commonly-used biocide (BCDMH) contains both bromine and chlorine atoms, but they are bonded via the nitrogen atoms rather than the carbon atoms.



2,2 - dibromo-3-nitrilopropionamide (DBNPA)



Bromonitrostyrene (BNS)

Organo-chlorine compounds

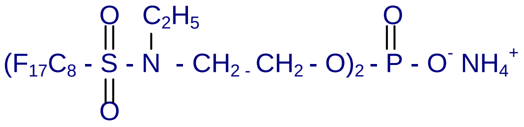
These are the most prevalent type of organo-halogen compound that can be found in papermaking systems. They originate from various sources:

- as biocides, although the use of some organo-chlorine biocides (eg chlorinated phenols such as PCP) has now been discontinued. One commonly-used biocide (BCDMH) contains both chlorine and bromine atoms (but not bonded to carbon).
- various organo-chlorine compounds (notably phenolics) may be present as contaminants in the papermaking system due to a previous history of pulp exposure to chlorine or to old manufacturing practices. These are commonly measured as AOX. Examples of now-discontinued organo-chlorine papermaking chemicals are pentachlorophenol, which used to be used as a preservative in some papers and polychlorinatedbiphenyls (PCBs), which used to be used in the coating of carbonless copy papers.
- chlorinated paraffins which are used as the dispersion medium for the colour-forming capsules in some carbonless copy papers.
- by-products such as a dichloropropanol in polyamide-epichlorhydrin wet strength agents and in some cationising agents such as CHPT.

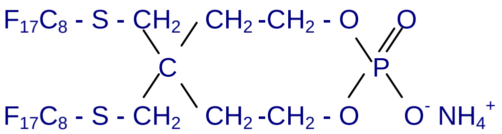
Organo-fluorine compounds

These compounds, sometimes referred to as fluorochemicals, are organic molecules with a carbon-fluorine (C-F) bond and are used in papermaking to impart oil and grease resistance to paper products. They represent an alternative technique to the traditional methods used to make papers such as glassine and vegetable parchment. These chemicals are principally applied at the paper surface (size press, calender water box or coater) than at the wet end, although the latter is possible.

The fluorine atom confers a highly hydrophilic character on the molecule, which enhances the natural oleophobic (hydrophilic) character of cellulose. A number of different chemistries have been used, but one of the most common types, the phosphate esters based on perfluoro-octanylsulphonates (see formula below at left) have been withdrawn from the market due to their non-degradability and environmental persistence. Other chemistries using the perfluoro-octanyl group (see example at right below) are still used.



$$(F_{17}C_8 - \overset{O}{\underset{O}{S}} - \overset{C_2H_5}{N} - CH_2 - CH_2 - O)_2 - \overset{O}{P} - O^- NH_4^+$$



The above types are available as solutions which may contain solvents such as iso-propanol. The other type of fluorochemical used for the same purpose are polymers based on acrylates, which again contain groups such as the perfluoro-octanyl (C_8F_{17}) or perfluoro-heptanyl units (C_7F_{15}). The fluoro-acrylates are produced as emulsions and can incorporate hydrophobic groups so that the product can be used to confer both water and grease resistance. Addition rates of both types are up to about 5 kg/tonne paper.

Organo-halogen compounds

These are organic compounds containing a halogen atom, but they may not necessarily possess a carbon-halogen bond. Organo-chlorine and organo-bromine compounds are used in papermaking as biocides and organo-fluorine compounds to impart grease resistance. Other organo-halogen compounds present in papermaking (mainly organo-chlorine compounds) may originate from pulp bleaching with chlorine-containing chemicals and from residues in recovered paper.

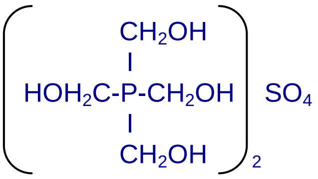
Organo-nitrogen compounds

This is a general term for the wide range of organic compounds containing nitrogen, most commonly based on amine or amides structures. As the presence of a nitrogen atom (either in a tertiary or quaternary form) is the main technique used to introduce a positive charge into an organic molecule, there are many organo-N compounds in papermaking:

- cationic polymers such as polyacrylamides, polyethyleneimines, polyamines, polydadmacs, cationic starch and polyvinylamines
- biocides such as quaternary ammonium compounds and guanidine derivatives.
- other quaternary ammonium compounds used as softeners
- urea, which is present in urea-formaldehyde resins and is used as a solubiliser for dyes and FBAs
- protein which have various applications in papermaking
- melamine-formaldehyde resins for the wet strengthening of paper
- polyurethanes for the surface sizing of paper

- dyes and fluorescent brighteners
- dye fixatives such as dicyandiamide
- FBA quenchers based on imidazolines.

Organo-phosphorous compounds



$$\left(\begin{array}{c} CH_2OH \\ | \\ HOH_2C\text{-}P\text{-}CH_2OH \\ | \\ CH_2OH \end{array} \right)_2 SO_4$$

These are organic compounds containing phosphorous, but relatively few are used in papermaking. There are two types:

- the organo-phosphonates with a P - C bond, some of which are used as scale inhibitors.
- the organo-phosphates with a P - O - C bond, two examples being:
  - the biocide tetrakishydroxymethylphosphonium sulphate (THPS) (see formula above).
  - in natural potato starches and in other starch esters.

Organo-silicon compounds

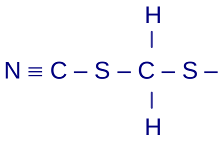
These are organic compounds containing silicon with a Si - C bond and feature in two types of papermaking chemical:

- as silicones in defoaming and anti-foaming agents
- as release agents used in release papers.

Organo-sulphur compounds

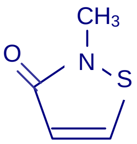
These are organic compounds containing sulphur and feature in two classes of papermaking chemical:

- organic biocides, two examples being methylene bisthiocyanate (MBT) and isothiazalones such as the one shown at right below. Some organo-sulphur compounds are also used as preservatives.
- fluorescent brighteners and anionic dyes through the presence of sulphonate groups.



$$\begin{array}{c} H \\ | \\ N \equiv C - S - C - S - C \equiv N \\ | \\ H \end{array}$$

MBT



2-methyl-4-isothiazolin-3-one

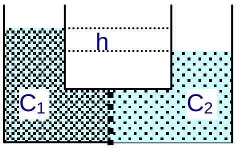
- organo-sulphur compounds are also present as lignosulphonates in sulphite pulps.

Orthokinetic

This is a type of particle aggregation process where the forces bringing particles in contact are caused by shear-induced velocity gradients. The other type of particle aggregation process is perikinetic aggregation.

Osmotic pressure

When two solutions are separated by a semi-permeable membrane (through which only the solvent can diffuse), the chemical potential is higher on the side with the highest concentration. In the diagram at right, $C_1 > C_2$, so, in order to try to equalise the chemical potentials either side of the membrane, water will pass through the membrane from the right-hand side (with the lowest concentration/potential) to the left-hand side (with the highest concentration/potential). This passage of water can be stopped by applying a counter pressure to the water on the side with the highest concentration and, when $C_2 = 0$, this is called the osmotic pressure (= h as a column of liquid).



Where there is pure solvent (water) on one side of the membrane, the van't Hoff equation applies:

$$\text{Osmotic pressure, } \pi = nRT/V = cRT$$

where n = moles of solute, V = volume, c = molar concentration

R = gas constant and T = temperature (^oK)

In papermaking, pulp fibres can be treated as if they were a semi-permeable membrane or, in fact, a polyelectrolyte gel due to the presence of charged groups within the fibre wall. In accordance with the Donnan theory, there is a higher cation concentration within the fibre wall than in the bulk solution (ie the fibre wall is the left-hand side of the above diagram) and the resultant osmotic pressure causes water to flow into the fibre wall, which enhances swelling.

Oxidation

In chemistry, this is one side of the overall process of transferring electrons between substances where the oxidation of one substance is always accompanied by reduction of another substance. An oxidising agent like oxygen has the ability to accept electrons as follows:

$$½O_2 + 2H^+ + 2e^- \rightarrow H_2O$$

These electrons can be donated by a reducing agent like hydrogen:

$$H_2 \rightarrow 2H^+ + 2e^-$$

and the overall reaction can be written as $H_2 + ½O_2 \rightarrow H_2O$ in which the hydrogen is oxidised and the oxygen is reduced to water. The ability of the reaction to proceed is determined by its redox potential. There are various oxidising chemicals used in papermaking.

Oxidised starch

These starches are produced by treatment of a starch suspension with a suitable oxidant, traditionally sodium hypochlorite, whilst keeping the temperature (20-40^{o}C) well below the gel temperature. The oxidant partly depolymerises the starch molecules, which lowers the viscosity of the resultant starch solution and converts some of the $-CH_2OH$ groups to $-COOH$ (carboxyl) groups, which reduces their retrogradation tendency. The degree of substitution of commercial oxidised starches is 0.01-0.04 corresponding to charge densities up to -0.25 meq/g starch. These starches have been widely used as a coating binder because of their ability to confer a very low high-shear viscosity on the coating mix, which gives good runnability. The starches produced by in-mill thermo-chemical conversion of purchased native starches are somewhat similar in character, but less anionic.

The drawback of the hypochlorite-oxidised starches is that they contain undesirable chlorinated-organic by-products, typically 20-100 mg/kg for potato starches and 60-400 mg/kg for maize/corn starches. The drawback of all oxidised starches added to the paper surface is that, like all non-cationic starches, they contribute significantly to wet end dissolved organics on the recycling of starch-containing broke and, because of their charge character, they also contribute to anionic trash.

Oxidising agents

These chemicals act as electron acceptors in the oxidation process. Oxidising chemicals used in papermaking include:

- ammonium persulphate, which is used to produce in-mill thermo-chemically converted starches
- chlorine or sodium hypochlorite, which are used as water disinfectants and bleaches, but where the active species is hypochlorous acid, and also for broke repulping

- chlorine dioxide, which is used mainly as a bleaching agent for some virgin chemical, but also as a water disinfectant and biocide
- hypobromous acid, which is formed in situ from sodium bromide and sodium hypochlorite
- hydrogen peroxide, which is used as a bleach, as a biocide and to produce in-mill thermo-chemically converted starches
- oxygen, which is used as a bleaching agent for some virgin chemical and deinked pulps
- ozone, which is used as a water disinfectant and possibly an on-machine biocide
- potassium monopersulphate, which is used to disperse wet strengthened papers on repulping.

Oxidising biocides

This is one of the two categories of biocide chemicals used to control microbial problems at paper mills. Those in use or with potential for use are:

- chlorine or sodium hypochlorite, which is mainly used for water disinfection
- sodium hypobromite, which is again mainly used both for water disinfection
- bromochlorohydantoins, which are widely used on-machine
- chlorine dioxide, which is used for disinfection of fresh and recycled waters and on-machine
- ammonium bromide, which is a relatively new chemical for on-machine use
- hydrogen peroxide or peroxy compounds such as peracetic acid, which is used on-machine
- ozone, which is occasionally used for water disinfection, but is still at the development stage as on-machine biocide.

Oxalic acid

This is a simple dicarboxylic acid (HOOC-COOH) which is generated in sulphite pulping. Oxalate salts (eg calcium oxalate) can cause deposits.

Oxolation

In contrast to olation, this is the term for molecules in which oxygen forms bridges in a polymer chain as takes place in the polymerisation of aluminium ions from added alum.

Oxygen

Oxygen is the lead element in Group 16 of the Periodic Table. It is a diatomic gas (O_2) and oxygen atoms are also present in a combined form in most papermaking raw materials. This ubiquity means that the elemental composition of most paper products will be headed by oxygen.

Molecular oxygen is an oxidising agent and this property underlies its various roles in pulping and papermaking. Oxygen is used in the bleaching of deinked pulps, but its much more prevalent role as a bleaching agent is with virgin chemical pulps, where it has two separate applications:

- in a separate oxygen bleaching (or delignification) stage which precedes the more powerful bleaching agents such as chlorine dioxide and ozone. This stage is operated under alkaline conditions (pH 12-13) and removes at least 50% of the unbleached pulp's lignin, thus lessening the load on later bleaching stages. The effects of oxygen on the level of charged substances in Kraft pulps is shown in the sections on bleached Kraft pulps, ECF pulps and TCF pulps.
- as an auxiliary chemical (sometimes with hydrogen peroxide) to reinforce the alkaline extraction stages.

Within the papermaking process, molecular oxygen is only present incidentally through air being dissolved or entrained in the liquid phase. However, both these processes are important as dissolved oxygen provides an essential element in the metabolism of bacteria and entrained oxygen (as part of entrained air) has an adverse effect on drainage of the papermaking stock and the formation quality of paper. The solubility of oxygen is governed by Henry's Law. Its equilibrium concentration with atmospheric O_2 is about 9 mg/l at 25°C, but decreases to about 6.5 mg/l at 50°C. This decline in solubility with increased temperature is very important in relation to the onset of anaerobic microbiological activity.

In aqueous systems that do not contain added oxidising or reducing chemicals, the presence of dissolved oxygen is important in maintaining an oxidising environment and preventing the development of reducing conditions. This is desirable in papermaking as anaerobic conditions lead to reducing reactions, usually microbiological in nature, that are undesirable. The relevant oxygen couples are:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \text{ where } E_H{}^o \text{ (redox potential) } = +1.2 \text{ volts at } 25^oC$$

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \text{ where } E_H{}^o \text{ (redox potential) } = +0.4 \text{ volts at } 25^oC$$

The difference in the standard electrode potentials indicates that oxygen loses some of its oxidising power as the pH increases with an actual potential for this couple of about +0.6 volts at pH 7, 25°C and the normal level of atmospheric oxygen. This is an important factor in the redox intensity of waters within the pH range seen on paper machines, where the electrode potential would drop from about +1 volt at pH 4 to +0.75 at pH 8. These redox reactions involving water are important as they define the redox and pH conditions in which water is stable and also effect corrosion reactions. It is interesting also to note that, as the standard potential for chlorine is greater than that that for dissolved oxygen, chlorine should be able to oxidise water to oxygen. This is a good example of a situation where a reaction is thermodynamically predicted, but does not take place as its kinetics are very slow in the absence of suitable catalysts.

Ozone

Ozone is a triatomic gas (O_3) and is a very powerful oxidising agent with the following half-cell reactions under acid or alkaline conditions:

$$O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O, \text{ where } E_H{}^o \text{ (redox potential) } = 2.07 \text{ volts at } 25^oC$$

$$O_3 + H_2O + 2e^- \rightarrow O_2 + 2OH^-, \text{ where } E_H{}^o \text{ (redox potential) } = 1.24 \text{ volts at } 25^oC$$

Due to its high reactivity, ozone is always produced on-site by the passage of an electrical discharge though air or pure oxygen.

Since the decline in the use of chlorine for bleaching chemical pulps, ozone is one of the oxidants that has found increasing use as a bleaching agent to produce both TCF and ECF bleached chemical pulps. It is usually used under acid conditions (pH 2.5), where its oxidising power is greatest, at doses of 2-4 kg ozone/tonne pulp. Ozone has also been used for bleaching/decolorising at one or two wood-free deinking mills, where it has the advantage of destroying the fluorescence from brightening agents.

To date, ozone is little used in papermaking, but it is known to be used by some mills for disinfection and/or oxidation of dissolved iron/manganese salts in fresh waters. Research on its use as an on-machine biocide has demonstrated its efficacy for microbial control, but high doses (up to 300 mg/l) are needed.

p

This refers to the transformation of a parameter into its negative logarithm (usually base 10), which is often used in physical chemistry.

$$pX = - \log_{10} X \text{ or } X = 10^{-pX}$$

Examples of the use of this transformation are pH and pK values.

PAC

This is an abbreviation for poly-aluminium chloride.

Packaging papers/boards

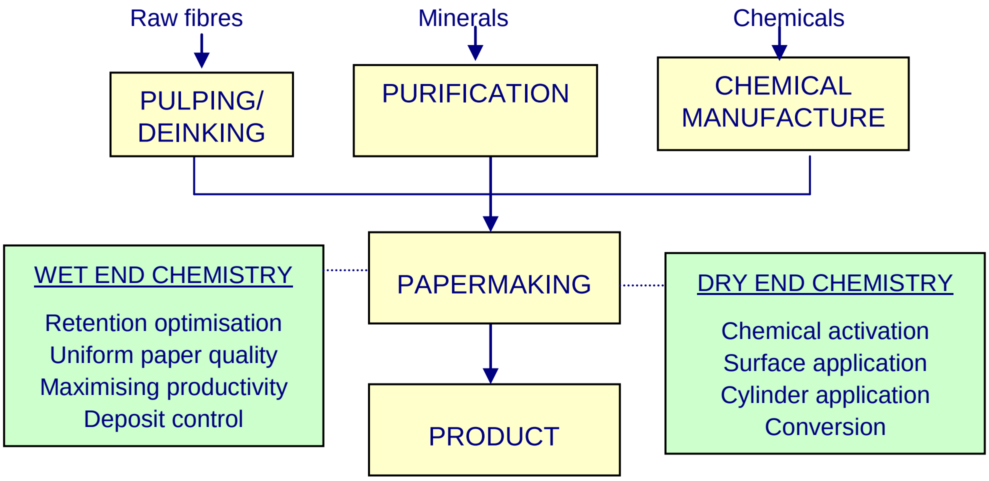
This is the single largest category of paper/board products, accounting for close to 50% of global production. It is also the sector with the largest overall use of recovered paper. The main packaging grades are:

- corrugated case materials, which are sub-divided into linerboard and fluting medium
- carton boards, there being four main grades
  - folding boxboard made from a mixture of chemical and mechanical pulps and used largely for food packaging and display
  - solid bleached board, made from bleached chemical pulps and used largely for packaging of pharmaceuticals and luxury goods such as cosmetics
  - solid unbleached board, made from unbleached chemical pulps and used widely in the packaging of many goods where appearance is less critical, eg beer bottles and cans.
  - white-lined chipboard, made from largely recovered paper with a deinked grade as the liner and widely used for general packaging of goods such as frozen foods, toys, shoes, etc.
- packagings specifically for liquid fillings ("liquid" packagings)
- bag and wrapping papers
- sack papers.

The key product requirement for all packaging grades is strength, notably in the form of stiffness and there are many specific testing procedures for the different packaging categories. Increasingly, packaging grades are required to convey information so printability may also be important.

Paper chemistry

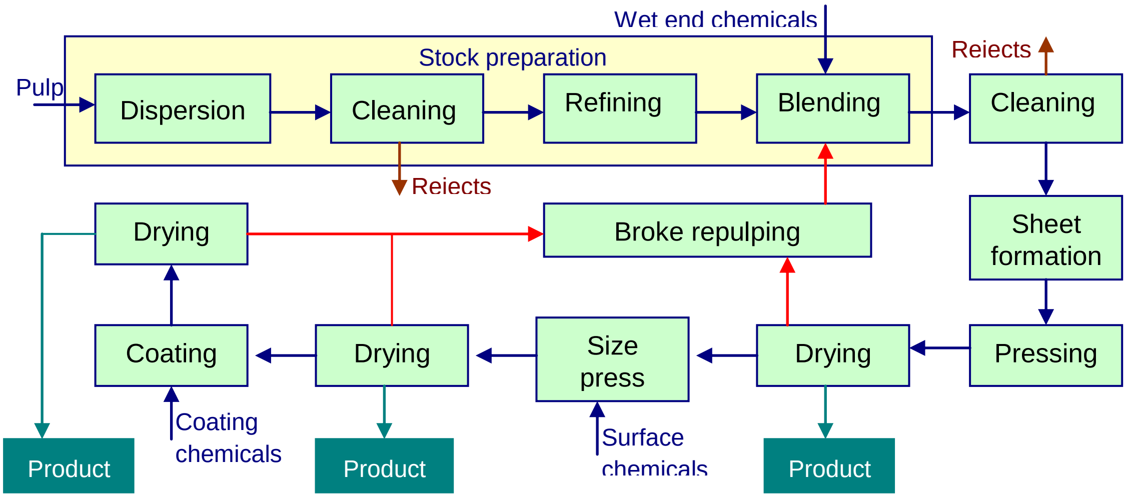
Paper is a complex material in which chemistry features throughout the manufacturing sequence (see summary figure below).



As is evident in the above picture, paper chemistry brings together the chemical aspects of three distinct phases in the manufacture of finished paper products:

- the chemistry of raw materials
    - pulp from raw fibres where chemistry plays an important role in the manufacture of all chemical pulps made from virgin fibres and in the manufacture of those recycled pulps that are deinked
    - fillers where chemistry does not play an important role for most natural fillers (eg clays), but is more important for the more speciality grades(eg titanium dioxide)
    - all other non-fibrous materials where chemistry plays a critical role.
- the chemistry of the papermaking process
    - chemistry of the wet end up to the drying section
    - chemistry of the dry end forward from the drying section
    - chemistry of converting paper into its final form for use.
- the chemistry of the product which integrates all the previous processes, but which is rarely specified or considered in any great detail by the user.

Papermaking



Papermaking is essentially a filtration (or thickening) process in which the paper base sheet is produced from a suspension of various materials, the composition of which depends on the grade being made. Much of the chemistry of the wet end of the papermaking process is directed at maximising the retention of these materials consistent with acceptable paper quality and machine runnability. Other chemicals may be added to the paper surface by spraying, by immersion at a size press and by coating. These chemicals are well retained during their application, but losses occur as a result of spillages, wash-ups and through the re-use of machine broke.

The fibrous raw material normally enters the paper mill as baled virgin pulp or recovered paper or loose recovered paper. Stock preparation is the general term for converting the as-received pulp to the right condition and composition for making into that grade of paper and usually comprises the initial slushing, mechanical treatment and blending with other materials. These are usually carried out as batch or semi-batch processes, although mechanical treatment of the fibre is performed continuously as the fibre suspension is pumped between upstream and downstream tanks or chests.

Firstly, the pulp has to be dispersed uniformly to form a 4-6% suspension in water by vigorous stirring in a circular tank with a bottom, high-speed rotor. Large debris such as baling wire and large plastics can be removed at this stage. High consistency pulping (10-12% solids content) is increasingly being used to reduce energy consumption or to prevent the comminution of contaminants in recovered paper and thus facilitate their removal by screening. The first cleaning stage shown in the diagram above is usually only present on machines using non-deinked recovered paper, where the higher level of contaminants demands several cleaning stages early in stock preparation (see this diagram for more details). Where deinked pulp is used, these processes would normally form part of the preliminary deinking system.

Mechanical treatment of the pulp is a crucial stage at most paper mills, although the pulps used to make some grades (eg tissue) may only receive minimal treatment ("deflaking") in order to preserve desirable papermaking characteristics such a softness and bulk. Mechanical treatment processes are known as beating or refining. Beating is an older batch process little used today as most mills use continuous refiners. There are two main types of refiner - the conical refiner and the disc refiner, both of which involve a ribbed or grooved surface moving against a second stationary surface with similar ribs or grooves. In passing between the two surfaces, the fibres are shortened and "fibrillated" thus increasing their strength, but impairing their drainage and retention characteristics. The consistency of the fibre suspension during refining is 3-3.5%.

After refining, the pulp suspension is blended in the "machine chest" with other pulps, which invariably includes machine broke and perhaps other recovered materials (see recycled pulp). Where present, other pulps may have been through a similar or slightly different treatment process, but the level of refining is often specific to a particular pulp type. Other wet end additives are usually added at about this location, but often directly to the thick stock after the machine chest unless a longer contact time is required. The relative location for the dosing of different additives can be very important to their retention and functionality in the system (see dosing and dose-response effects).

The remainder of the papermaking system before the paper web is formed is known as the "approach flow" system. The consistency of the papermaking stock is regulated at around 3% solids content before it is diluted at the "fan" pump to papermaking consistency using recycled "backwater" (water already drained through the formation wire). More details of the water system are described under water closure. Papermaking consistencies vary from about 0.02% (200 mg/l) for long-fibred stocks making lightweight products through 0.3-0.5% (3-5 g/l) for fine papers up to about 1% (10 g/l) for boards and some other grades.

In the "approach flow" system, the stock is cleaned in a 3 or 4 stage hydrocyclone system and finally by screening. Other chemicals, such as some retention aids, are often added continuously to the "thin stock" shortly before it is delivered to the "wet end" of the paper machine itself. There are many different types of paper machine, which differ in exactly how the fibrous suspension is converted into a paper web, the main ones being:

- the conventional Fourdrinier machine for making all paper grades

  This comprises a flowbox (often called a headbox) to apply the stock uniformly to a continuous horizontal wire or fabric, which is wrapped around two rolls (the "breast" roll and the "couch" roll) plus other smaller rolls to tension the wire on its return (see this diagram for representation). The flowbox is usually pressurised in order to deliver the required flow through the narrow opening (slice) onto the forming fabric. The flowbox may be equipped with rectifier rolls to mix the flowbox contents or mixing can be done hydraulically. Water is removed from the consolidating sheet by gravity drainage followed by suction drainage, so that by the time the sheet reaches the couch roll, it has a dry solids content of 15-20%. Some machines may have a second flowbox for applying a second layer on top of the first and other machines may be fitted with a drainage unit mounted above the wire in order to improve sheet uniformity.

- ☐ vat machines for board making

  Here the thin stock is pumped to a small tank that contains a fabric-covered drum or cylinder, which rotates either in the same or the opposite direction as the carrying fabric. There are usually several such vats for making multi-ply boards. Sometimes, the board machines may include a combination of fourdrinier sections (usually for the liner and back plys) and vats for the middle plys.

- ☐ gap formers for making graphical and packaging papers

  The stock from the flowbox is projected into the gap between two forming fabrics that converge together so that water is removed concurrently from both sides. This gives rapid sheet consolidation and produces a paper with excellent even-sidedness.

- ☐ specialised formers for making tissue and towel grades

  There are many different types in this category (eg roll and crescent formers), but all are characterised by a very short drainage zone due to the ultra-light weight of these products.

In nearly all cases, the formation stage is followed by a press section, where further water is removed by applying pressure to the sheet in contact with absorptive fabrics ("felts"). This is normally performed by passing the paper web in the nip between two large press rolls. Each press part contains 2-4 such nip arrangements. The sheet leaving the press section generally has a dry solids content of 40-55% depending on sheet characteristics and press design. The higher solids contents are achieved by techniques such as "extended nip" and "hot" pressing.

The residual water in the web is normally removed by passing it over steam-heated drying cylinders, which are traditionally arranged in two staggered rows one above the other. Some papers are dried in contact with large single cylinders known as "Yankee" cylinders when used for tissue/towel grades and MG ("machine glaze") cylinders when used to produce smooth MG papers. After drying, most paper machines are equipped with an array of on-line sensors to measure key sheet properties such as grammage, brightness, colour, etc. Some papers (eg newsprint) may be further treated in a calender stack (a vertical train of finely-ground cylinders) to improve surface finish.

As mentioned in the first paragraph of this section, many machines also have dedicated equipment for the surface application of chemicals at a size press or coating station. Size presses are always incorporated as an intermediate stage within the drying section, whereas coating may take place on-line at the end of the paper machine or as a separate off-line operation with its own final drying section. Paper machines can be up to about 10m wide and run at speeds up to about 2000 m/minute with individual production capacities up to around 0.5M tonne per annum. At the other extreme are older or more specialised machines making a few 1000 tonne per annum at speeds measured in 10s of m/minute. These differences in speed of operation have a major influence on some of the chemical interactions taking place at the wet end and during water removal.

Paper microbiology

This characteristic is important to the hygienic quality of all papers, but is critical for grades such as tissue, towel and food-contact packagings. The microbial content of papers is obviously influenced to some degree by the microbial inputs (bacteria and fungi) to the papermaking system, but the key factors are the microbial load entering and the temperature-time profile in the drying section. On most paper machines, the contact time during high temperature drying is adequate to kill virtually all the micro-organisms except heat-resistant bacterial spores. Some data from various reel samples is shown in the table below. In this study, about 90% of the identified bacteria were various *Bacillus* species, the most common being *Bacillus subtilis*, but *Clostridium* species can occasionally be detected. Even these bacteria are killed by prolonged exposure to high temperature, but the decimal reduction time is much longer than the time available in drying (eg about 10 minutes for *B. subtilis* at 100^{o}C).

Product	Type of pulp used	Bacteria (CFU/g)
Food wrap papers	Virgin pulp	1.5×10^3
Sweet wraps	Virgin pulp	2.7×10^3
Facial tissue	Virgin pulp	1×10^2
Toilet tissue	Virgin pulp	2×10^2
Hand towels	Recycled pulp	$1\text{-}9 \times 10^2$
Industrial towels	Recycled pulp	5×10^3
Light-weight board	Virgin pulp	1.7×10^3
Light-weight board	Recycled pulp	$1\text{-}3 \times 10^5$
Heavy-weight board	Recycled pulp	$1\text{-}3 \times 10^5$

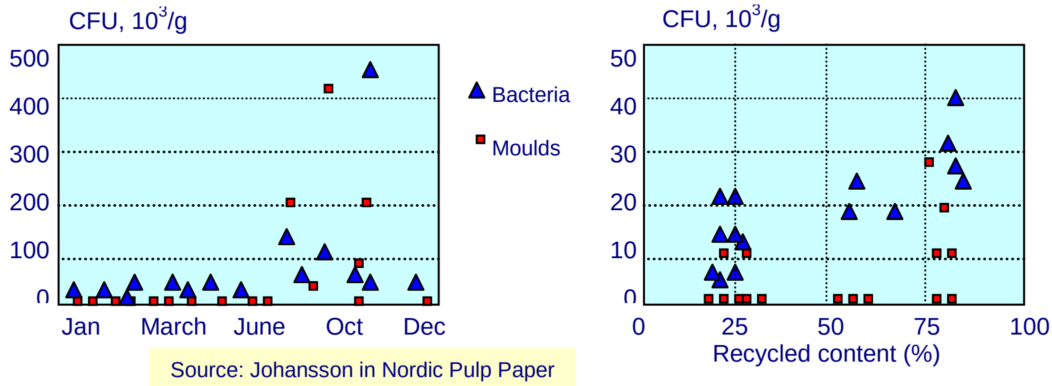
Note: CFU = colony-forming units

Source: Holt, DM in Proceedings 7th International Biodeterioration Conference, Cambridge, 1987.

Although not sterile, paper products thus have a high microbial quality at the reel on the paper machine, but are then open to considerable infection from later handling practices and from air-borne contaminants. Provided that the paper is kept reasonably dry, this high bacterial quality is maintained, but the growth of fungi is more of a problem as they are able to survive and grow at much lower moisture levels. As the fungal levels in reel samples are zero for most of the time, any subsequent growth is through later contamination and the most common species found in papers are common air-borne fungi such as *Penicillium*, *Aspergillus* and *Cladosporium* species. Some papers (eg label papers, wallpapers, etc) are treated with preservatives to stop fungal growth.

The issue of most concern in this area is probably the impact of recycled pulp on the microbial quality of papers. In the data tabled above, the highest bacterial levels are in papers made from recycled pulp. Other studies have tended to confirm this general picture, eg data from Finnish mills in the mid-1990s showed bacterial levels mainly in the range of 1×10^2 to 4×10^3 CFU/g in papers made from virgin pulp, whereas papers made from recycled pulp contained levels mainly in the range 1×10^4 to 4×10^5 CFU/g. This study also showed that some papers (made from both virgin and recycled pulps) contained substances that gave positive results in a standard toxicity test (using luminescent bacteria) and in a standard mutagenicity test. (in this context, it is worth re-calling that substances in the extractives fraction of wood are deliberately toxic to protect the wood.)

This issue has also been investigated at a Swedish mill that made various grades of linerboard from varying proportions of virgin pulp (unbleached Kraft) and recycled pulp. As shown in the figure at left below, the samples contained relatively low levels of aerobic bacteria and fungi in samples taken during the Winter and Spring, but some contained much higher levels in Summer and Autumn. This difference was suspected to be due to microbial growth within the recovered paper fraction and, as shown in the figure at right below, the highest bacterial and fungal contents were associated with the higher proportion of recycled pulp. As would be expected, the vast majority of the bacteria in the products were spore-formers of the *Bacillus* species, including the pathogenic *B.cereus*. This parameter was the only one (in the paper) that (just) exceeded the Swedish guideline level for microbial content in various foods. This work and more detailed studies on this aspect by TEGEWA (the German Association for manufacturers of, amongst other things, paper auxiliaries) showed that there was no significant transfer of microbes from paper/board products to dry, moist or greasy food.



Source: Johansson in Nordic Pulp Paper Research J., 2001, 16, 1, 40-44.

Paper products

The generic term "paper" often includes products that are strictly boards (sometimes also called paperboards). The normal classification of paper (and board) products breaks them down into the following principal grades:

- printing/writing (graphical) papers, which is the second largest category of paper products
- packaging papers/boards, which is the largest category of paper products
- other boards, one of the more important being plasterboard
- tissues and towels, which are quite small in tonnage terms (but much bigger when judged in monetary value)
- miscellaneous and speciality papers such as
    - papers with closed surfaces such as greaseproof papers (vegetable parchment and glassine) and tracing papers
    - papers with open surfaces such as filter papers and cigarette tissue.

The key properties of paper products vary with grade, but the physical characteristics always outweigh their chemical and microbiological qualities.

Paper properties

The properties of paper products that determine their end use are largely physical properties, which can be categorised under the following headings:

- strength properties, which are crucial to the functionality of all paper products
- optical properties, which are particularly important for printing, writing and copying papers
- surface properties, which play a role in paper's strength and optical character, but also in its appearance and the user's subjective assessment of its "quality".
- dimensional properties, which are basic metrics, but subject to some variability due to the chemistry of pulps.
- miscellaneous properties such as permanence, porosity, resistivity, etc.

Chemical characteristics of the paper are not commonly needed to be known in order to define a paper product's functionality, but many chemical parameters can be measured if needed, the more common being pH, ash content and sulphate content. For specific grades, chemical purity is important such as the metal content of photographic papers and the electrolyte content of insulating papers. The hygienic quality of paper is important to some degree for all papers as they are invariably handled at some stage and this aspect is obviously critical for grades such as tissue, towel and food-contact packagings. This is also affected by its chemistry, but the prime concern is its microbiological quality, an often-ignored attribute for most paper products.

Paper quality

The term "quality" used to be applied rather loosely to paper (and other) products, but the introduction of quality management systems (such as the ISO 9000 series) has imposed a little more discipline. Quality is most commonly defined as the "satisfaction of customer needs" and should not be used to rank (different) products in terms of their level of functionality, eg product A is not of higher quality than product B because it has, for example, a higher strength, but both products are of equal (acceptable) quality if they meet the (different) end-use specifications. Paper quality is usually judged by measuring key paper properties, a particularly important facet of paper quality being its uniformity within individual reels and across several reels of identical product. Non-achievement of the required quality may be caused by many factors (some chemical), but all will result in the production of machine broke, which may then further complicate process chemistry when it is recycled to the wet end.

Parenchyma cells

These are simple cells that store food materials within the wood xylem.

Particle aggregation

The state of particle aggregation is very important in two areas of papermaking:

- in wet end chemistry, where the objective is to promote the controlled aggregation of particles to optimise retention and drainage of the wet end stock and deliver a uniform paper quality
- in coating chemistry, where the objective is to minimise aggregation and maintain a uniform suspension of dispersed pigment particles within the coating matrix.

Positive particle aggregation is thus required only at the wet end, where there are particles with many different characteristics, but where their natural particle size distribution is very important in terms of particle aggregation mechanisms:

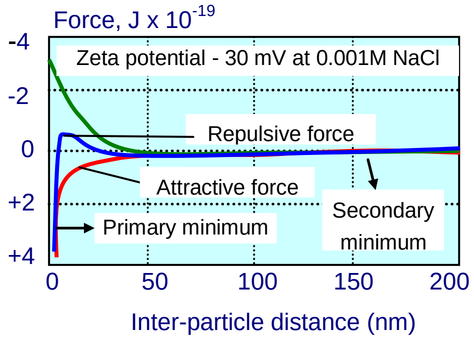
- the fibre fraction of pulps

  Due to their large dimensions, this fraction does not require enhanced aggregation for improving single pass retention and drainage. In fact, the dominant issue for genuine fibres is to minimise their macro-flocculation in order to maintain acceptable formation quality of the paper.
- the fines fraction of pulps plus any added fillers

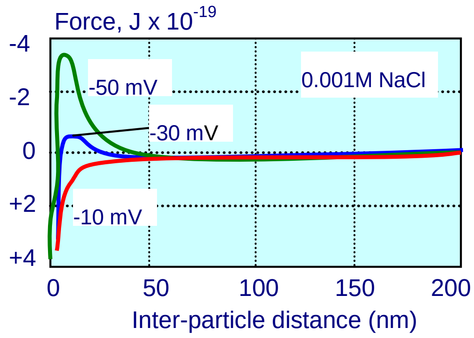
  Due to their colloidal dimensions, this fraction requires enhanced aggregation for improving their single pass retention and, on some machines, also for improving stock drainage. This is achieved through the addition of chemicals that function as retention and/or drainage aids, but the formation quality of the paper still exerts an important influence on the extent of fines aggregation.

The language of aggregation processes for fine particulate materials can be somewhat confusing as some of the terms are used rather generically and also have somewhat different meanings to different specialists. Coagulation and flocculation are the two terms used to describe the aggregation of colloidal particles by added chemicals, but are often used inter-changeably with one another although they have specific meanings for different types of aggregation process. In order not to imply any particular mechanism, the term "aggregation" will be used in this document to denote the coming or deliberate bringing together of particles.

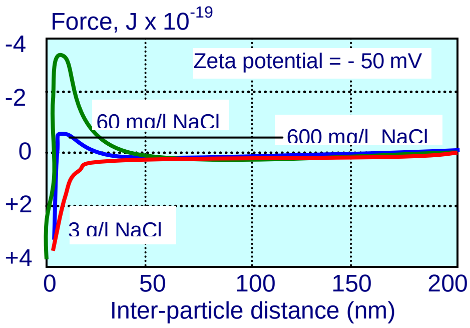
Fine particles remain as discrete entities or aggregate together depending on the relative strengths of the attractive and repulsive forces between them. At the wet end of the paper machine, the most important are the van der Waals attractive forces and the electrostatic repulsive forces. This is treated quantitatively in the classical DLVO theory named after the two sets of researchers (Dejaguin/Landau and Verwey/Overbeek) who independently developed it. Some examples of the effect of the principal variables in particle interactions are given below. One of the variables in the equations for both the attractive and repulsive forces is the size of the particle. As both forces are linearly dependent on the particle diameter, the net force also increases in a linear fashion, so no examples are given of this effect and all the examples below use a particle diameter of 200 nm.



As the electrostatic repulsive force diminishes as an exponential power of the inter-particle distance and the attractive force diminishes as the reciprocal of this distance, the net force is strongly attractive at close inter-particle distances (known as the primary minimum) and weakly attractive at a large inter-particle distance (known as the secondary minimum). This is shown at right for a moderately negative particle (zeta potential = -30 mV) in the presence of a low electrolyte concentration (as NaCl). At very close distances (<1 nm), there is a strong (Born) repulsion (not shown) due to overlapping of electron clouds. At intermediate distances, repulsion predominates and becomes stronger with increased particle charge, as described in the next example below.



The most obvious way to promote particle aggregation is to reduce the surface potential and hence the repulsive force. For the predominantly negatively-charged particles present in papermaking, this can be done using many cationic substances such as alum or cationic polymers. It can be seen here at left that the surface potential does not have to be reduced to zero to achieve a net attractive force, but in this particular case, a surface potential of ±10mV is enough to give a net attractive force.



The presence of electrolytes reduces the thickness of the electrical double layer, thus compressing the sphere of influence of the electrostatic repulsive force. Using sodium chloride as a typical electrolyte, we see here at right that quite moderate concentrations are able to make the net force attractive. If the electrolyte has a divalent counter-ion (ie calcium ions for a negatively-charged surface), the net force is made attractive at concentrations which are low enough to be exceeded in many papermaking systems. However, such aggregates have poor floc strength and would be too weak to withstand the shear forces present in most papermaking systems, so specific chemicals (retention aids) are used in most systems to generate aggregates of adequate shear resistance. Examples of retention improvements brought about solely by added electrolytes (such as that shown here for a bleached chemical pulp) are only possible on low-shear laboratory formers.

Aggregation can thus take place only if the particles can approach close enough for the attractive force to predominate. Particles thus have to possess some kinetic energy in order to be on a collision course with one another and to surmount the repulsive energy barrier (if present). Aggregation can occur via perikinetic forces caused by Brownian motion or via orthokinetic forces caused by shear-induced velocity gradients.

The kinetics of aggregation for like particles is a simple second order reaction in relation to the number of particles (n of radius a):

Collision rate, $J = -dn/dt = f.n^2$ which, on integration, gives $(1/n) – (1/n_0) = ft$

where n_o = number of particles

and the time for 50% of the particles to aggregate, $t_{1/2} = (fn_o)^{-1}$

For dissimilar particles, the situation is somewhat more complex and is usually modelled by a first order reaction in relation to the number of the smaller particles (n of radius a), where the concentration of the larger particle (N of radius A) is assumed to be constant :

$J = -dn/dt = f.n.N$ which, on integration, gives $\ln(n/n_0) = fNt$

and the time for 50% of the smaller particles to aggregate with the larger particles, $t_{1/2} = \ln2.(fn_o)^{-1}$

For perikinetic conditions, $f = \frac{2kT(A + a)^2}{3\eta Aa} = 8kT/3\eta$ for like-sized particles

For orthokinetic conditions, $f = 4G(A+a)^3/3 = 32Ga^3/3$ for like-sized particles

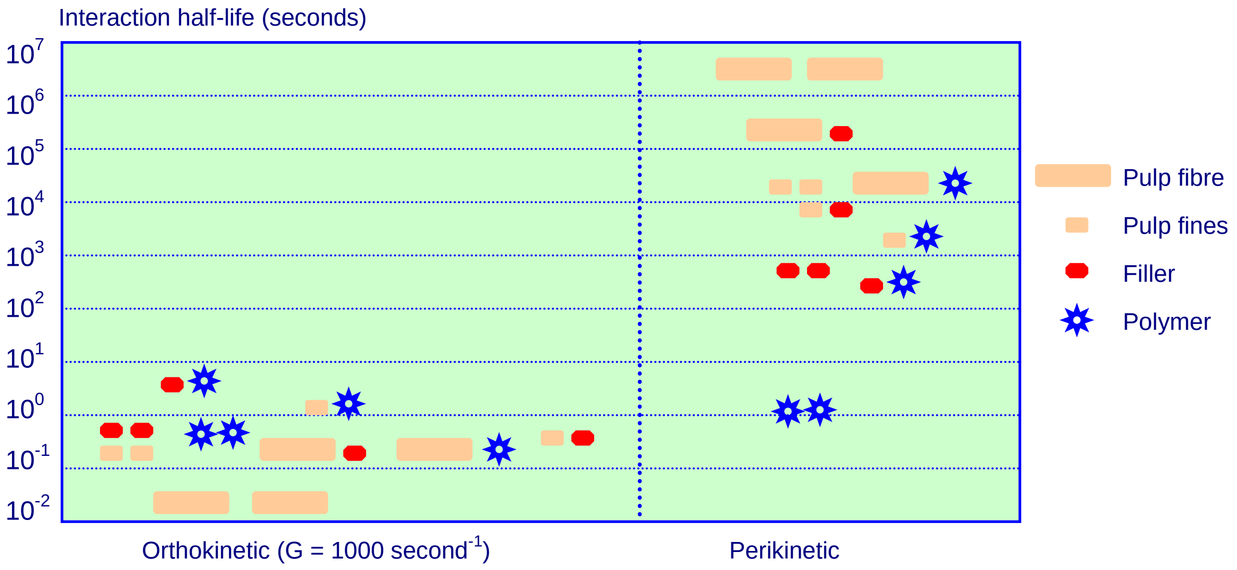
where G = shear rate, k = Boltzmann's constant, T = absolute temperature and η = water viscosity

When there is no energy barrier preventing close inter-particle approach, aggregation can take place quite rapidly, but, it is slower when there is a repulsive energy barrier. This is taken care of by introducing a "stability ratio" term, which defines the proportion of the collisions leading to permanent contact. Although shear is necessary for aggregation of larger particles, the resistance of the aggregated particles to further shearing (their floc strength) and their ability to re-aggregate together when the shear is removed are also important.

It can be useful to use these equations to give an idea of the ordering of wet end interactions when different types of material are present under both perikinetic and orthokinetic conditions. It should be emphasised that the actual results depend markedly on the actual concentrations involved and the actual level of shear. The latter affects not only the collision frequency, but also the breaking apart of any aggregates formed. The attractive forces between particles (van der Waals or electrostatic) are proportional to the particle diameter, but the hydrodynamic forces are proportional to the diameter^2 so they get larger as aggregates grow in size. If prolonged, these forces can lead to further re-arrangement of aggregated solids or transfer of adsorbed solids as shown here for a polyacrylamide.

The following example has been calculated for a thin stock sample containing the following materials:

Property	Pulp fibre	Pulp fines	Filler	Polymer
Equivalent spherical diameter (µm)	100	10	2	0.2
Material density (kg/m^3)	500	500	2600	-
Mass concentration (g/l)	5	1	1	0.001
Particle concentration (number per litre)	2×10^{10}	4×10^{12}	7×10^{14}	1×10^{17}



It is often quoted that perikinetic collisions are only significant for particles/molecules smaller than about 1 µm in size and this is confirmed by the data shown in the figure above, where only the interaction between dissolved polymers (ie between an added cationic polymer and anionic trash) takes place within a timescale of seconds rather than minutes or longer. There is little difference between the time-scale of inter-polymer actions under perikinetic or orthokinetic conditions, each polymer molecule colliding with only about one other polymer molecule every second. The position of fibre-fibre interactions is markedly different, being the shortest under orthokinetic and the longest under perikinetic conditions. It is particularly pertinent to see that the fastest polymer interaction (apart from with other polymers) is with fibres so that the retention of fillers and pulp fines will be via their interaction with a polymer-adsorbed fibre (rather than of polymer-adsorbed filler with fibre). Fibres collide about 1000 times more with polymer molecules than do filler particles, but, because of the large number of polymer molecules, the collision with polymers is the most common one for fillers.

When polymers are added to promote particle aggregation, the kinetic model for particle collision frequency has to be modified by introducing a term for its fractional surface coverage with polymer (C):

$$J = k.n^2.C.(1-C)$$

This equation predicts that the maximum flocculation occurs at 50% surface coverage (C = 0.5), which agrees with measurements of the maximum rate of flocculation for both patch and bridging polymers. In all types of polymer flocculation, particles may be re-stabilised by the addition of excess polymer. In the case of low molecular weight cationic polymers, complete coverage of the particle surface would lead to elimination of any negatively-charged patches and hence to repulsion between the fully cationised surfaces. Particle re-stabilisation like this can occur for various reasons:

- overdosing due to poor control of polymer dosing
- poor mixing at the point of polymer addition leading to localised high concentrations
- the build-up of polymers recycled in the whitewater or in the broke.

The above factors allied to the often imprecisely-known hydrodynamic characteristics of many paper machines make true optimisation of particle aggregation and chemical adsorption processes rather difficult. The above example indicated the kinetically-favoured interactions when all the competing materials were present at the same time, but an obvious way of controlling interactions is through managing the order of and delays between dosing of the various additives. The one constant is usually that the pulp has to be present first, but it is possible to pre-mix other additives (eg filler and another chemical) in a side-stream if this allowed a beneficial interaction between them that would not take place by adding either separately to the pulp, ie A +(B+C) is better than (A+B)+C or (A+C)+B.

Particle characteristics

In mass terms, the main raw materials used in papermaking are all particulate materials that do not dissolve under normal papermaking conditions - pulps, fillers, pigments and sizes. Minor (but not unimportant) fractions may dissolve because of their inherent water solubility (eg hemi-celluloses from virgin pulps and starches from recycled pulps) and others may dissolve unintentionally due to poor process control (eg calcium carbonate under localised acid conditions). A unique characteristic of insoluble particulate raw materials is that they have a surface which can interact with other particulates and with dissolved substances.

These interactions depend on the following primary characteristics of particulate substances:

- their particle size distribution, which is very wide for all pulps and fairly wide for fillers/pigments
- their particle shape or morphology, which is very variable and heterogeneous
- their surface chemistry in terms of particle charge and interfacial energy.

The simplest particle shape is the sphere, the diameter of which determines two important particle characteristics:

- the particle number/unit mass = $6/\pi\rho d^3$, where ρ = density and d = diameter

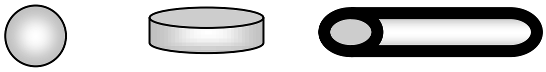
  The inverse cubic relationship between particle numbers and diameter means, for example, that there are 1000x as many 1µm particles as 10µm particles of the same total mass. This parameter is important in relation to the retention aspects of the papermaking furnish, ie achieving a high single pass retention becomes more difficult as the particle size gets smaller simply because there are more particles to aggregate together (see this example for fillers).

- the surface area/unit mass = $6/\rho d$

  The simple inverse relationship between specific surface area and diameter means, for example, that 1µm particles have 10x surface area of 10µm particles of the same total mass. This also means that the proportion of molecules in the particle's surface layer increases as the particle size reduces, reaching about 20% of the total at the bottom of the colloidal range. The specific surface area of particles is important in relation to several furnish properties, for example:

  - the adsorption of wet end additives, which is partly determined simply by the space available (see this example for cationic starch)
  - the amount of additive required to bring about certain functional effects in the paper such as the level of sizing or coloration.

Unfortunately, few particles in papermaking are perfect spheres, but the shape of minerals such as calcium carbonate and titanium dioxide is reasonably spherical. For other particulate materials in papermaking, a useful indication of the influence of particle size can be obtained by using simple model shapes for the rather more complex shapes of real fibre and other filler particles as shown in the picture at right.



Sphere for $CaCO_3$ Disc for clays Hollow tube for fibres.

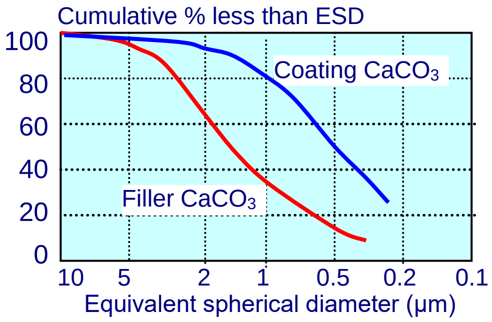
For irregular–shaped (anisometric) particles such as fibres and clays, it is impossible to assign a single number to define their size so it is normal to specify one dimension (eg the diameter of a disc or the length of a tube) and relate the other dimension to it. This defines the particle's aspect ratio, which, for a disc, is the ratio of the diameter to thickness and, for a rod or tube, is the ratio of length to diameter. The traditional technique for measuring particle size is sedimentation as the particle settling velocity can be related to particle size through Stokes' Law:

Particle terminal settling velocity, $V = k.(\rho_P - \rho_L).d^2/\eta$

where k = constant, ρ_P = particle density, ρ_L = liquid density, d = particle diameter, η = liquid viscosity.

For irregular–shaped (anisometric) particles, the particle size is expressed as the equivalent spherical diameter (esd), which is the diameter that a particle with the same settling velocity would have if it were a sphere. For disc- and rod-shaped particles, the esd is always less than the disc's diameter or the rod's length, eg for an aspect ratio of 20, the esd is about on third of the disc's diameter or the rod's length. For some mineral particles, their void volume is another important characteristic in terms of light-scattering for fillers and coating performance for pigments.

The particle size distribution of materials such as mineral fillers is usually defined by mass percentages below various particle sizes such as 2μ, 1μ, etc. The narrowness or steepness of the particle size distribution can be important for papermaking fillers and this can be defined in a single number as the ratio of the particle sizes at any two points in the distribution. Typical examples of such distributions are shown at right for two calcium carbonates.



A few examples are useful to illustrate some of the differences between papermaking raw materials, when compared on the basis of their mass, numbers or surface area, as shown in the following table. The effect of the stock fines content in terms of the proportion of particle numbers and surface area associated with the flowbox fines is shown here.

Type of particle	Dimensions	Number/g	Surface Area (m^2/g)	Wet end concentrations		
				Mass (g/l)	Number/litre	m^2/litre
Pulp fibre	Tube, 2mm x 20µ	1 x 10^{7}	1	5	5 x 10^{7}	5
Pulp fines	Tube, 2µ x 2µ	1 x 10^{12}	8	1	1 x 10^{12}	8
Clay	Disc, 2µ x 0.1µ	1 x 10^{12}	10	1	1 x 10^{12}	10
CaCO$_3$	Sphere, 2µ φ	1 x 10^{11}	3	1	1 x 10^{11}	3
Colloidal silica	Sphere, 5 nm φ	6 x 10^{18}	500	0.005	3 x 10^{16}	2.5
Polyacrylamide	-	-	-	0.001	6 x 10^{13}	-
Polyethyleneimine	-	-	-	0.01	6 x 10^{16}	-
Calcium ion	-	-	-	0.1	1 x 10^{21}	-

Particle charge

The chemical character of particles determines their charge characteristics when suspended in clean (ie deionised) water, but the actual charge in the papermaking system depends on their interaction with dissolved substances that originate from other sources. The particle charge in papermaking reflects the net impact of the following effects:

- ionisation of functional groups such as the carboxyl groups within the pulp matrix. The surface charge on pulps is zero at about pH 2.5 (the iso-electric point) and becomes increasingly negative as the pH is raised (see this figure). Some substances (eg the proteinaceous surfaces of bacteria) are amphoteric and thus can be positively or negatively charged depending on pH.

- dissolution of charged substances from pulps, thus transferring the charged material into the bulk solution where it becomes part of the anionic trash which may affect the adsorption of other charge-determining substances

- Adsorption of charged material (ions or polymers) from solution. Inorganic anions adsorb on surfaces more readily than cations as anions tend to be less hydrated in solution. Hydrophilic surfaces (such as cellulosic fibres) are often solvated with water molecules and adsorb materials less readily than do hydrophobic surfaces

- imperfections in the structure of some minerals leading to a charge imbalance within the mineral lattice, eg substitution of aluminium for silicon in a clay would lead to a negative charge on the mineral.

In most papermaking systems, the particulate surfaces have a similar charge character (usually negative) even though their underlying chemical character is very different. This is due to the adsorption of materials from solution, some of which may originate from one of the particulate materials (see this example for various fillers in the presence and absence of pulp). Some mineral materials have the somewhat unusual property of having some areas with a positive charge and another with a negative charge, eg bentonite and kaolin clays with their anionic faces and cationic edges. Even in such cases, each particle has a net negative charge.

The particle charge is a key variable that influences a number of important papermaking phenomena:

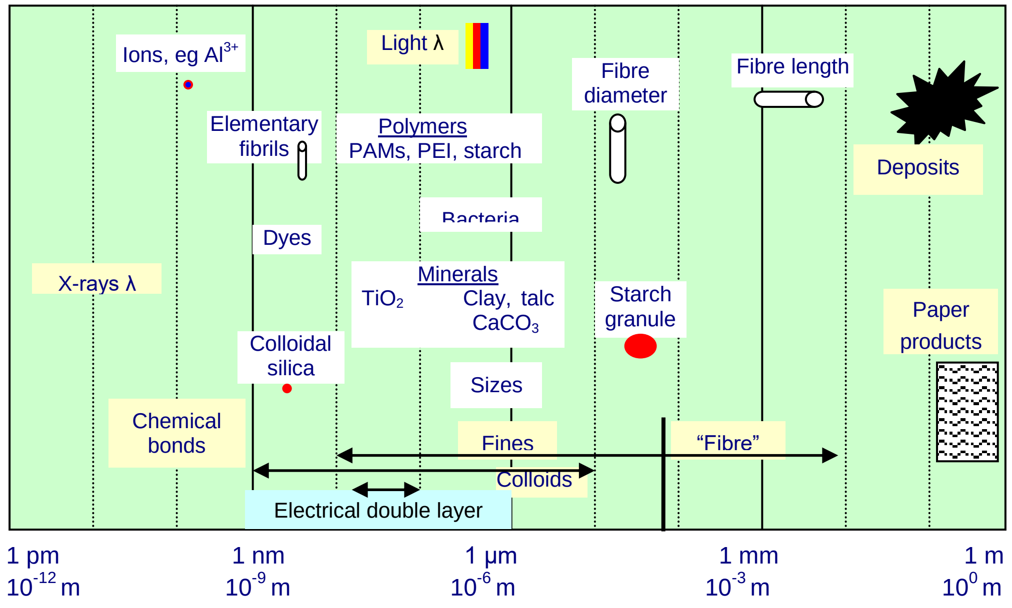
- the magnitude of the electrostatic force between particles, which is normally (in the absence of added chemicals) a repulsive force and can thus prevent particle aggregation. This is undesirable at the wet end, but desirable in coating.
- the adsorption of substances, normally those of opposite charge to that of the surface, ie substances with a positive (cationic) charge
- for pulps, the swellability of the fibres/fines, which in turn influences drainage and organics dissolution at the wet end and the strength of the paper.

The particle charge is measured either by an electrokinetic technique as a potential (eg zeta potential) or by a charge titration in charge units (such as Coulombs or meq) per unit mass. For porous particles like pulp fibres, the titrated charge may refer to two different charge values depending on the accessibility of the titrating substance:

- the surface charge, which is the charge determined by titration with a “large” polymer, usually a polydadmac of 0.2M Daltons molecular mass
- the total charge, which is the charge determined by titration with ions and “small” polymers, the later usually being an ionene of 8k Daltons molecular mass.

There are several examples in this document illustrating the difference between measured total and surface charges - here for some ECF bleached Kraft pulps, here for some ECF bleached Kraft pulps, here for a range of ECF and TCF pulps and here for range of mechanical and chemical pulps.

Particle size



As shown in the diagram above, the papermaking furnish contains particles with an enormously wide range of particle and molecular sizes. Whether added at the wet end or to the paper surface, most materials have colloidal dimensions, the prominent exception being the genuine fibre fraction within pulps. The particle size distribution of the wet end stock reflects the particle size distribution of the added raw materials as modified by the interactions taking place between the various particulate solids and added dissolved substances as the stock moves through the various wet end processes. Even when the chemistry of the stock is fixed (ie after the final chemical addition before web formation), the state of inter-particle aggregation continues to respond to changes in mixing and shear conditions.

The papermaking system (both at the wet end and in coating) is inherently polydisperse compared to the majority of systems used for theoretical study, which are usually monodisperse. Not only do the particulate materials have a range of dimensions, but the shape of many particles is irregular, eg long, narrow fibres and flat, platy clay fillers. The above diagram shows the common division of particulate components into "fibre" and fines, which can be performed using the Dynamic Drainage Jar or the traditional Bauer-McNett classification system. A more detailed breakdown of fibre length can be provided by image analysis techniques or specific commercial instruments.

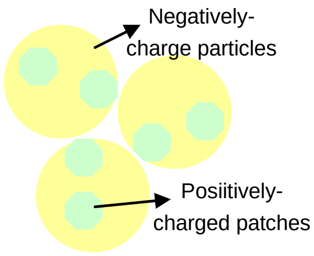
The above picture includes some of the papermaking additives that are present as dissolved molecules rather than as discrete particles. Many of these are polymers, the molecular dimensions of which vary with the chemistry of the liquid phase, notably with the concentration of electrolytes. The actual molecular size of polymers within the papermaking system can be evaluated using filtration through very fine ultrafiltration systems or by gel permeation chromatography (see solute exclusion).

PASS

This is an abbreviation for poly-aluminium silico-sulphate.

Patch flocculation

As shown in the picture at right, patch attraction is a type of particle aggregation brought about by certain types of polymer. Low molecular mass (<1M Daltons) polymers with a charge of high density and opposite to that of the particle (ie cationic polymers for anionic pulps and fillers) adsorb strongly on the surface in a flat conformation and, unlike high molecular weight polymers, are not long enough to be able to form bridges between particles. At a sufficiently high polymer dose, the whole particle surface could be covered with cationic polymer, but this would be of little value to particle aggregation as the particle suspension would then by stabilised by repulsion between cationic particles. When enough polymer has been added to cover about half the particle surface, there are still areas of negative charge and attraction can thus occur between patches of the negatively-charged surface on one particle and patches of positively-charged, polymer-covered surface on another. As in the case of bridging (but to a much greater extent), there will be some contribution to flocculation by simple charge neutralisation, but the dominant attractive force is the patch attraction. There are several types of cationic polymer used for this type of particle aggregation in papermaking, eg polyethyleneimine, polydadmacs and polyamines.



An important characteristic of patch-type flocs is their ability to re-flocculate after they have been broken down by shear. Patch-flocculated suspensions are disrupted at lower shear levels than bridged flocs, but the still-present patches can re-associate to re-establish flocculation once the shear is removed (see this figure for comparison of polyacrylamide versus polyethyleneimine). Thus, although the flocculation produced by patch-type polymers is inherently weaker, the flocculating ability of the non-retained particles in the whitewater can be re-harnessed on the next pass.

PCBs

This is an abbreviation for polychlorinatedbiphenyls.

PCC

This is an abbreviation for precipitated calcium carbonate.

PCP

This is an abbreviation for pentachlorophenol.

Pectin

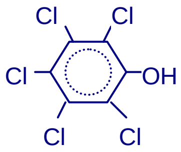
This is a component of wood which is present mainly in the middle lamella and the primary cell wall. It is a polymer largely of galacturonic acid, but with small amounts of other sugars such as arabinose and rhamnose. Some of the galacturonic acid units are present as methyl esters, the proportion in this form depending on the wood species. Hydrolysis of the methyl esters occurs under alkaline conditions (such as in peroxide-bleaching of a mechanical pulp) leading to greater dissolution of pectin substances with a strong anionic character (see data for spruce pulp) . These substances contribute to anionic trash, but are precipitated by calcium ions. One possible treatment uses pectinase enzymes.

PEI

This is an abbreviation for polyethyleneimine.

Pentachlorophenol

This chemical (formula at right) can be present in traditional chemical pulps that have been bleached with high levels of chlorine gas, but not in ECF or TCF pulps. It used to be used as a preservative in some paper products, but this has been discontinued on environmental grounds due to high aquatic toxicity.



Pentose

These are monosaccharides having 5 carbon atoms, two being important in papermaking - arabinose and xylose, which are both present in various hemi-celluloses.

PEO

This is an abbreviation for polyethyleneoxide.

Peracetic acid

This material is a mixture of acetic acid and hydrogen peroxide and can act as an oxidising agent with the following half-cell reaction:

$$CH_3COOOH + 2H^+ + 2e^- \rightarrow CH_3COOH + H_2O \text{ where } E_H^o \text{ (redox potential) } = +1.06 \text{ volts}$$

It is used in papermaking as an on-machine biocide.

Perikinetic

This is the term for a type of particle aggregation process caused by Brownian motion, but it is only significant for particles below about 1µ in size. The other type of particle aggregation process is orthokinetic aggregation.

Periodic Table

This is the table of all the known chemical elements, which currently numbers 110. The originator of the Table was the Russian chemist, Mendeleev, in 1872, at which time there was only 65 known elements. As can be seen below, it is organised into vertical columns (the 18 groups of elements with similar characteristics) and horizontal rows (the periods), which increase steadily in atomic number (the value in each box, which is the number of protons in the nucleus and of electrons surrounding it) and in atomic mass (not stated in the table, but equal to the number of protons and neutrons in the nucleus). It is not the total number of electrons, but the number of valency electrons, that determines the generic properties of an element and the group to which it belongs.

Groups containing elements significant to papermaking are listed briefly below:

❑ Group 1 (excepting hydrogen) - the alkali metals

Each of these elements has a single electron in the outer “s” orbital and this is easily lost to give the monovalent cation. Only the sodium ion is present at significant levels in papermaking.

❑ Group 2 - the alkali earth metals

Each of these elements has two valency electrons, which, with the exception of beryllium, are easily lost to give the divalent cation. The most significant element in papermaking is calcium, but magnesium is present in some raw materials and barium to a lesser degree in others.

❑ Groups 3 to 10 - the transition elements

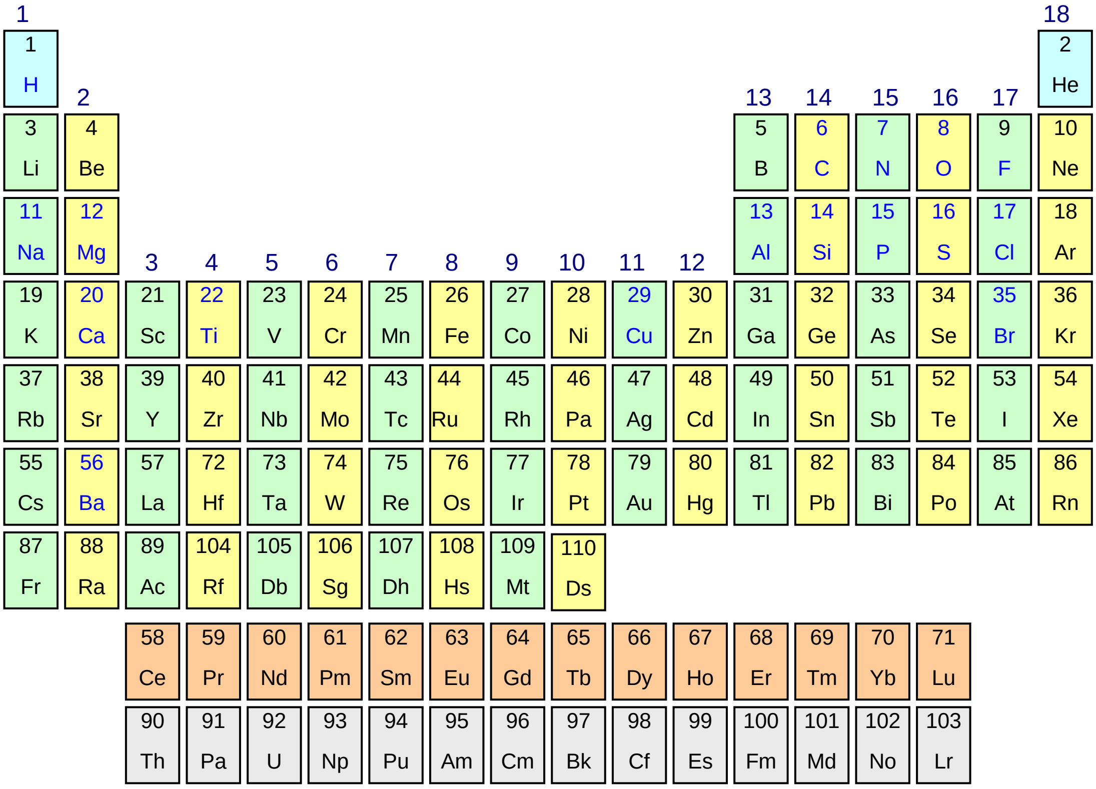
This represents a wide range of largely metallic elements that form cations with varying valencies due to the ease of ionisation of the d electrons. The most significant element to papermaking is titanium in terms of its oxide, but zirconium (Zr) salts have also found a use as a crosslinker for certain substances and chromium complexes have been used to confer grease resistance on paper.

❑ Groups 11 and 12

The elements in these two groups bear some superficial similarity to the elements in Group 1 and 2 in terms of their main valency, but are more complex due to the availability of the d electron shells. Only one element features in any papermaking materials and this is copper, which is present in some dyes.

❑ Group 13

The decreasing metallic character across the table is evident in the wide range of covalent compounds formed by aluminium, the group's second element and a common element in various guises in papermaking. The lead element boron is only found in one form (borates) that may be seen in papermaking systems, but this is not usually from direct addition.



1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pa	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Dh	108 Hs	109 Mt	110 Ds								
		58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu		
		90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr		

- Group 14

  This group best illustrates the changing metallic character down the Periodic Table as it goes from the non-metallic carbon, the basis of organic chemistry, to the metallic lead. It also includes silicon, which appears in several papermaking raw materials.

- Group 15

  The increasing acidity of the oxides across the table is very evident with the first element, nitrogen, which plays an important role in many papermaking raw materials. In its covalent compounds, the uncharged atom is trivalent, but the positively-charged nitrogen ion is isoelectronic with carbon and can form 4 single bonds. This is invariably the source of cationicity in many papermaking additives. The second element, phosphorous, is also present in several papermaking raw materials.

- Group 16

  Whereas the ubiquitous oxygen only has a valency of 2, sulphur can utilise two 3d electron orbitals to produce 6 sp^3d^2 hybrid orbitals and thus increase its valency to 6 (as in SF_6). Both elements, but particularly oxygen, are present in many papermaking materials and occur together in sulphate and hydrosulphite ions.

- Group 17 - the halogens

  The halogens are all strongly electrophilic although this does decrease substantially down the Group. The three leading halogens (fluorine, chlorine and bromine) are present in some papermaking chemicals.

- Group 18 - the Noble (formerly Inert) gases

  As their name indicates, these are all gases and, because of their complete electron shells, very stable with few chemical reactions (none known for helium, neon and argon).

Permanence

This term refers to the ability of papers to retain their functional characteristics over time. It is mainly used in relation to the loss of strength of papers (embrittlement) caused by the adverse effect of any acidity in the paper on cellulose. This can be prevented by maintaining an alkalinity reserve of at least 2% calcium carbonate. Other properties of paper may change over time, two further examples being the darkening of wood-containing papers exposed to light (brightness reversion) and the loss of sizing (size reversion).

Permanent hardness

This is the fraction of any water hardness that is present as calcium or magnesium sulphate/chloride and is classed as permanent as it cannot (unlike temporary hardness) be removed by boiling. It can be removed by addition of soda ash:

$$CaSO_4 + Na_2CO_3 \rightarrow 2CaCO_3 + Na_2SO_4$$

Both calcium and sulphate ions are generally undesirable in papermaking, although calcium ions can be beneficial in certain circumstances.

Permeability

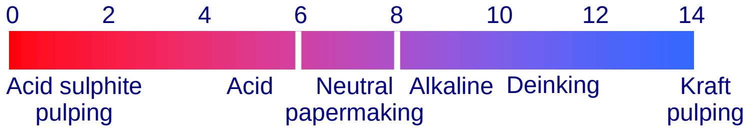
This an alternative term for the porosity of paper.

PGW

This abbreviation stands for pressurised groundwood pulp or pulping process.

pH

The pH of the papermaking system is an important variable that can have significant effects on many facets of the process and paper quality.



Three papermaking pH domains can be identified (see diagram above for comparison with the pH in other pulping processes):

- acid papermaking (pH < 6)
- neutral papermaking (pH 6-8)
- alkaline papermaking (pH > 8).

The pH value is a measure of acidity or alkalinity and is defined as the negative logarithm (base 10) of the hydrogen ion concentration:

$pH = -\log[H+]$ where $[H+]$ is measured as molarity or, more strictly, as activity.

An alternative way of looking at this is: $[H+] = 10^{-pH}$

In an aqueous system, the ionisation of water defines the neutral point where the concentrations of hydrogen and hydroxyl ions are equal. The ion product of water (K_W) is defined as follows:

$$K_W = [H+][OH-])$$

At 25°C, $K_W = 1 \times 10^{-14}$, ie $pK_W = 14$ and $pH = pOH = 7$.

As K_W changes with temperature, the neutral point changes from about pH 7.5 near water's freezing point to pH 6.6 at 50^{o}C. In systems where the pH isn't controlled, the operating pH is dependent on the balance of acid inputs (eg many pulps) and alkaline inputs (eg calcium carbonate filler), mediated by the natural buffer capacity of the fresh water which depends on its temporary bicarbonate hardness. Shifts in pH can also occur due to microbiological activity, which generates acid species such as carbon dioxide and, under anaerobic conditions, organic acids such as acetic acid. A shift in pH can itself lead to changes in the microbial flora, a good example being the greater predominance of fungi compared to bacteria in acid compared to neutral systems.

The pH of the papermaking stock is an important wet end parameter as it influences the ionisation of certain groups and thus their charge character:

- the charge on the particulate surface increases with raised pH generally leading to higher (more negative) zeta potentials (see examples for bleached kraft pulp here, for fillers here, for the effect of alum on pulp charge here and for the effect of rosin mobility here) and higher titratable charge contents (see example for bleached Kraft pulp here and for a chemimechanical pulp here)
- the charge of chemical additives changes in a similar way, anionic chemicals becoming more anionic and some cationic chemicals less cationic as the pH is raised (see example here for the effect on alum hydrolysis, here for the effect of pH on starch cationicity, here for the effect of pH on AKD emulsion charge, here for an example of the effect of pH on starch retention and here for the effect of pH on pitch ionisation).

The net effects of these changes determines the overall impact on system properties such as pulp swelling, single pass retentions and the functionality of additives such as rosin. The pH of the paper web during drying is also important for some papers, notably those sized with AKD, where high pH aids curing (see this example). The pH may be specified for some paper products that are to be stored for a long period (eg acid-free archival papers). Unless it has been subject to attack by acidic gases in the atmosphere, the pH of the paper should be similar to that at the wet end when it was made, but the precise value will depend on the measurement technique.

Wet end pH is easily measured manually by a calibrated glass electrode or on-line by a glass or an antimony electrode. The glass electrode is normally kept free from accumulated debris by the use of an ultrasonic cleaner and some commercial antimony electrodes use a rotating carborundum stone. The pH of papers may be measured by a hot or cold extraction of the water-soluble substances and pH measurement on the resulting solution or by contacting the electrode with the wetted paper surface. These values will be different due to different chemical compositions and dilution levels.

Phosphorous

This Group 15 element is not very common in papermaking materials, but it does occur in the following:

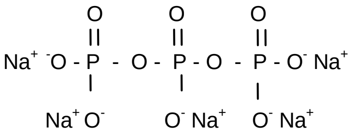
- phosphate groups present in anionic and natural potato starches
- polyphosphates used as release agents and scale inhibitors
- organo-phosphorous compounds such as phosphonates and phosphonium salts used as scale inhibitors and biocides.

Phosphates

The phosphate group occurs in a number of guises, orthophosphate and polyphosphate being the most common in papermaking. The simple orthophosphate anion (PO_4^{3-} in its fully ionised form) is present in natural potato starches or synthesised starch phosphate esters, where it is attached to carbon 6 as $-H_2C-O-PO_3H_2$. The very different acidic character of the three hydrogen atoms in orthophosphoric acid was described here.

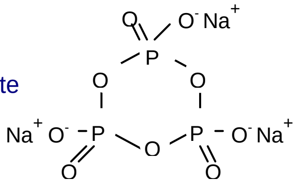
There are various forms of polyphosphates, a basic sub-division being between the linear polyphosphates themselves and the cyclic polymetaphosphates, the formulae of two common examples being shown below.

Sodium tripolyphosphate
$Na_5P_3O_{10}$



$$\mathrm{Na^{+}\;{}^{-}O-\underset{\underset{Na^{+}O^{-}}{|}}{\overset{\overset{O}{\|}}{P}}-O-\underset{\underset{O^{-}Na^{+}}{|}}{\overset{\overset{O}{\|}}{P}}-O-\underset{\underset{O^{-}Na^{+}}{|}}{\overset{\overset{O}{\|}}{P}}-O^{-}Na^{+}}$$

Sodium trimetaphosphate
$Na_3P_3O_9$



Polyphosphates are used for several applications in papermaking:

- as release agents in creping formulations
- as chelants in bleaching with sodium hydrosulphite
- as chelants for scale prevention.

Phosphonate

This is the term for those organo-phosphorous compounds where there is a P-C bond unlike the P-O-C bond in organo-phosphates. They are used as anti-scalants, one example used in papermaking being amino-tri-methylenephosphonic acid (ATMPA) which has the formula, $N(CH_2PO_3H_2)_3$.

Physical chemistry

This is one of three main branches of chemistry and is formally defined as the study of the physical changes associated with chemical reactions and the dependence of physical properties on chemical composition. It has many sub-divisions, but the following are relevant to paper chemistry:

- colloid chemistry, which is the chemistry of the interactions between very small particles and large molecules
- electrochemistry, which is concerned with the interconversion of electrical and chemical energy
- kinetics, which is the study of the rates of chemical interactions
- thermodynamics, which is the science of the different kinds of energy and the transformations between them.

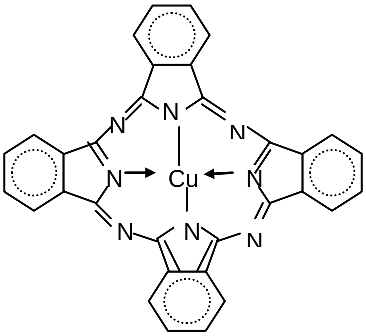
Picking

This term is used for the lifting or loss of fibres from the paper surface during pressing or paper drying. It is caused by poor surface strength and bonding of fine particles. The term "linting" is used for the similar effect of the loss of fibres or fillers from the paper surface during printing.

Pigment

This term has two somewhat different meanings in papermaking:

- it may refer to any particulate substance used to modify the natural coloration of a paper or
- it may refer to the white, largely mineral, materials used as the basis of normal aqueous coating.



In the first instance, it comprises coloured minerals such as iron oxides and cadmium sulphide and can include organic pigments such as carbon black and those based on phthalocyanine (see formula at right). The main advantage of using solid pigments, instead of dyes, for coloration is their good light-fastness, but this is counter-balanced by low tinctorial strength. In order to achieve a uniform coloration, the pigment must be well distributed and this demands a very fine particle size. This is often achieved by the incorporation of dispersants to give a high solids content paste. The small particle size and the presence of dispersants can give rise to poor and variable wire retention, even with the use of a retention aid, leading to a marked 2-sidedness in the paper. For this reason, coloured pigments are not as widely used at the wet end as dyes, but are applied more in coating applications. Coloured pigments account for less than 10% of colorant use in the paper industry, the rest being supplied by water-soluble dyes.

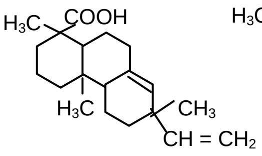
The second definition of pigments include all the materials, that are also used as wet end fillers, but also a few materials only used for coating. The main materials used as white coating pigments are:

- kaolin clay, which is the dominant coating pigment globally, albeit less than it used to be
- calcium carbonate, which is continually increasing its market share, particularly in Europe
- talc, which, although third in the list, is well-behind clay and carbonates
- titanium dioxide, a speciality pigment with the highest opacity
- aluminium oxide, a speciality pigment with high absorption characteristics
- aluminium hydroxide, a speciality pigment with flame retardant characteristics
- satin white, a speciality pigment used to give very high gloss
- barium sulphate, a speciality pigment used in photographic papers
- calcium sulphate (gypsum), a speciality pigment with a growing market in LWC grades
- plastic pigments, speciality pigments with much lower density than mineral pigments.

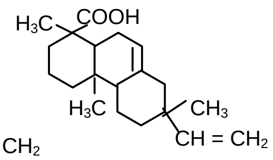
The pigment accounts for at least 80% of the coating solids by weight, but the pigment's volume fraction is equally important to its role in the coating. The volume fraction depends on the packing ability of the particles, which depends on a combination of their particle shape, particle size distribution and anisometry. Because of their strong anisometric character, clays exhibit the lowest void volume.

Pimaric acid

This is one of the two groups of monocarboxylic acids that comprise the resin acids, which is part of the extractives fraction of wood. Some resin acids may, after pulping, remain with the papermaking pulp as part of its pitch fraction. Pimaric acids are also one of the main components of rosin size. There are only two acids in this group, which are distinguished from the abietic acids by having methyl and vinyl groups (rather than an iso-propyl group) in the third ring. The two pimaric acids are shown at right.



Pimaric acid



Isopimaric acid

Pine

This is a type of softwood tree, which is widely used to make mechanical and chemical pulps for papermaking. Pine species tend to have a high extractives content, which has been quoted for Pinus sylvestris as 2.5-5% of the dry wood, being composed of about 50% neutral substances (mainly fatty acid esters), about 20% free fatty acids and about 30% resin acids.

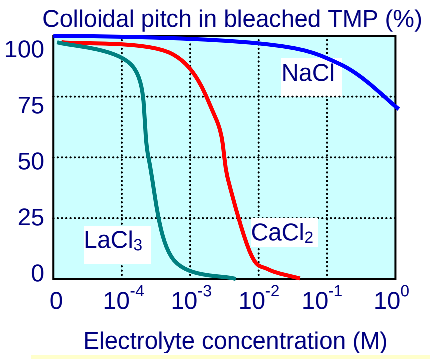
Pine can contain very high levels of carboxyl groups from resin acids, but the total carboxyl content is quoted at about 150 μeq/g, of which only about one third (50 μeq/g) is fully accessible to cation exchange before hydrolysis and about two thirds (90 μeq/g) after hydrolysis. The glucuronic acid content is about 80 μeq/g, ie about half of the total charge.

Pitch

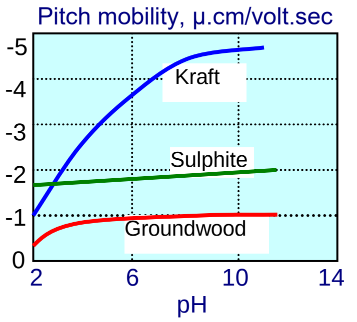
Pitch is one of various sets of problematic substances in papermaking, in this case their main problem being one of deposition. Pitch is a generic term for a complex mixture of materials in virgin pulps, which originate from the extractives fraction of the original wood. This contrasts with another type of problematic substance, white pitch, which is associated with the recycling of coated papers.

Chemically, pitch is a mixture of saturated/unsaturated fatty acids/esters, resin acids and neutral unsaponifiable compounds. Softwoods (particularly pines) have much higher levels of extractives than do hardwoods. Despite the lower overall pitch levels in hardwoods such as birch, they contain more unsaponifiable material, which is the fraction most difficult to treat chemically. With any wood species, the severity of pitch problems depends on the logging season. Ageing of the wood encourages enzymatic hydrolysis and oxidation reactions which improve the solubility of unsaponifiable pitch components and hence their removal during pulping. This process is faster during summer months. Ageing is more important for hardwoods as they contain higher levels of fatty acids in the form of esters than do softwoods. This effect can be augmented by the addition of specific fungi to the wood during storage in the woodyard.

Some of the pitch precursors are removed during the pulping/bleaching processes, but the nature and quantity of pitch passing forward in the pulp to the paper machine depends critically on the nature of the pulping process. As the extractives fraction has limited water solubility in its natural state, mechanical pulps contain most of the pitch precursors that were present in the wood in a largely intact form. In spruce TMPs, the galactoglucomannans remaining with the pulp help to stabilise the colloidal pitch particles by a steric stabilisation mechanism, but this tends to break down when the pulp is bleached so that the pitch can then be aggregated by electrolytes (see figure below at left).



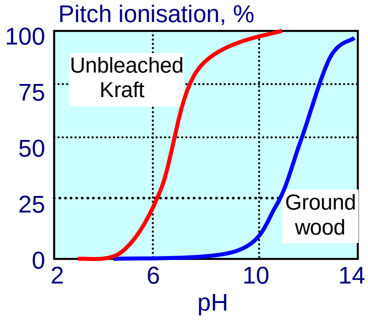
Source: Sunberg K at COST E14 Symposium, 2000, Hungary.



Source: Allen, Pulp Paper Canada 1975, 76, 5, 70-77.

The more severe physico-chemical conditions during chemical pulping may remove much of the pitch precursors, but there are significant differences in pitch content between different types of chemical pulp. In sulphite pulping processes, the fatty acid esters are hydrolysed to the free acids and glycerol, but the acidic conditions allow no saponification so the pitch remains in a weakly anionic form (as shown in the above figure at right). Unbleached sulphite pulps thus contain high pitch levels. Bleaching of sulphite pulps should lower pitch levels through some saponification during the alkaline extraction stages, but bleached sulphite pulps are not produced in large quantities today.

The alkaline conditions in Kraft pulping allow the hydrolysis of fatty acid esters and saponification of fatty acids to their sodium soaps, which then act as surfactants for dispersion of the neutral pitch components. However, the solubility of the fatty acids is limited by the high ionic strength of the pulping liquor and by their reaction with calcium ions to precipitate the calcium soap. Calcium ions are abundant in the pulping liquor from their presence in the wood. Even when the high pH of the pulping liquor is reduced as the pulp is washed, the ionisation of the Kraft pulp pitch at neutral pH is sufficient to allow the reaction with calcium ions (see figure at right). The retention of the calcium soap with the unbleached pulp increases with the calcium concentration as this destabilises the colloidally dispersed soap particles, which initially have sizes of 0.1-0.2 microns.



Source: Allen, Tappi J., 1988, 71, 1, 61-64.

The multi-stage bleaching of chemical pulps (particularly Kraft) is a very effective means of removing residual pitch pre-cursors due to the alternating alkaline extraction stages. The disadvantage of traditional chlorine bleaching of chemical pulps is that many substances are chlorinated and this includes residual extractives. As the chlorinated extractives are less soluble in the alkaline extraction stages than unchlorinated extractives, the use of ECF bleaching, in which chlorination reactions are minimised, facilitates removal of extractives from the unbleached pulp.

The impact of residual extractives on pitch problems in papermaking depends not only on their content in the pulp, but also on their chemistry. From a quantitative angle, mechanical and unbleached sulphite pulps head the list, but Kraft pulps are not without their problems due to the ionisation pattern of the residual substances. As seen in the two figures above, the pitch-forming substances in Kraft pulps ionise at a much lower pH (in the acid/neutral region most common on paper machines), which means that colloidal pitch particles can be easily precipitated by calcium ions. Such problems are exacerbated by differences in pH, for example between the stock and shower waters, which can lead to pitch deposition on wires/felts. In mechanical pulps, some of the pitch remains within the fibre cell wall and is only released to become a potential problem when adequate hydrodynamic shear forces are present on the paper machine. The released pitch particles can then aggregate aided by chemical changes induced by pH shifts and the presence of certain cations such as calcium.

Pitch problems can be controlled using the same hierarchy of techniques summarised generally for all deposit-forming substances. In terms of pitch problems, these are:

- selecting raw materials with the lowest possible content of pitch and their precursors

  This technique is feasible for pitch in virgin pulps and pitch specifications are already used for market pulps such as bleached Kraft.

- so far as it is practicable, optimising machine operation (without chemical addition) firstly to minimise formation of depositable pitch and then to minimise its actual deposition.

  This could include control of pH to minimise ionisation of fatty/resin acids, which is relevant mainly to Kraft pulps. This would mean maintaining a low pH, which is practicable on water systems for showers, but may be less so at the wet end depending on the chemistry required for other chemicals, eg sizes.

- dosing of specific control chemicals.

  There are several alternative approaches to minimise pitch deposition:

  - addition of adsorbents such as talc to the pulper

  Talc is perhaps the most widely-used pitch control chemical due to its ease of use and the need for little tight control, provided that it is added as early possible in the system so that the individual pitch particles are allowed to adsorb on the talc before agglomeration takes place. Good single pass retention of the talc/adsorbed pitch is essential to prevent build-up and possible desorption. Talc doses are around 1% on pulp. Cationic talc has been shown to give better pitch removal than ordinary talc (see this example) and, although not as widely used, other adsorbents for pitch control are bentonite (see this example with bentonite and polydadmac) and modified kaolins.

  - addition of alum to the thick stock

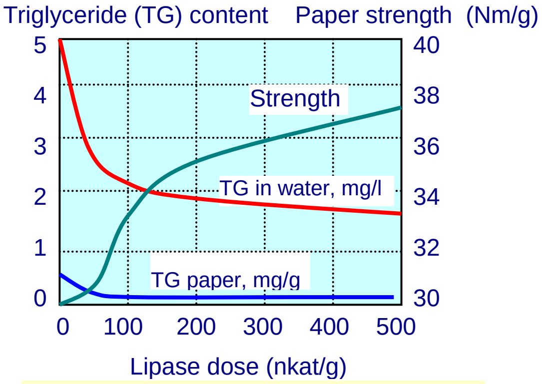
  The use of alum is obviously most suited to machines already operating under acid conditions and this technique is thus quite widely used on newsprint machines. Normal practise is to add a high dose (about 1% on fibre) to the thick stock at the pulper at fairly low pH (<4.5). The high aluminium concentration in the thick stock (ca 25 mg Al/l) is diluted to 5-10 mg Al/l in the thin stock at a higher pH (>5), a concentration/pH regime found to be optimum for newsprint mills. However, alum tends to affect adversely some paper properties such as brightness and strength.

  - addition of cationic polymers to stock or to formation fabric

  Addition of cationic polymers at the wet end has been used to promote stabilisation of pitch particles (see this example for polydadmac) and adsorption on fibres and this technique has also been successfully adapted to spray technology. Solutions of cationic polymers are spayed continuously onto the area where pitch (or other tacky deposits) are accumulating and the modified surface prevents pitch attachment, ie a sacrificial layer is formed. The polymer is dosed via the conventional showers on the wire or on press felts.

  - addition of enzymes

  This technique involves the addition of lipase enzymes which are able to hydrolyse the fatty acid esters. This work was initially carried out in Japan where the addition of lipase to a groundwood newsprint furnish reduced pitch deposits, pitch holes in the sheet and the quantity of talc used. Further work has confirmed the reduction in triglycerides (see figure at right), but has also shown a significant increase in sheet strength for TMP furnish. There were no significant changes in sheet brightness or light scattering.



Source: Mustranta in Nordic Pulp Paper Research J., 2001, 16, 2, 125-129.

- addition of dispersants to keep the pitch particles apart in the liquid phase.

This approach has been used successfully to control moderate pitch problems, but suffers from the major disadvantage that it allows the pitch to build-up in the system and this may cause other problems (eg foaming) on machines with very closed water systems.

pK value

This is the negative logarithm (base 10) of the equilibrium constant.

Plasterboard

This is a speciality board grade, which is made on multi-ply machines usually from a 100% recycled pulp furnish. The chemistry of these machines bears some resemblance to that of machines making linerboard and fluting due to the similarity of the pulp furnish and the fairly high degree of water closure. However, one difference is the wet end sizing chemistry, which is usually based on ASA rather than rosin or AKD.

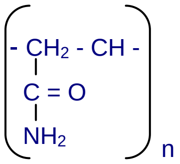
Plastic pigments

This term includes a small number of materials that, like mineral pigments/fillers, are used for their opacifying characteristics. They have the added characteristic of being much lighter than minerals and thus not increasing the paper's density. They include urea-formaldehyde and polystyrene pigments

Poise

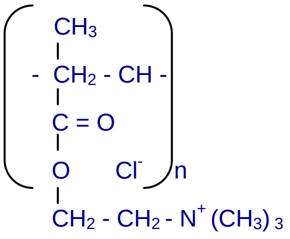
This is the unit of viscosity, which has the units of 10^{-1} Newton.second/m^2, which is identical to 10^{-1} kg/second.m and 10^{-1} Pa.second.

Polyacrylamides



$$\left(\begin{array}{l} -CH_2-CH- \\ \quad\ | \\ \quad C=O \\ \quad\ | \\ \quad NH_2 \end{array}\right)_n$$

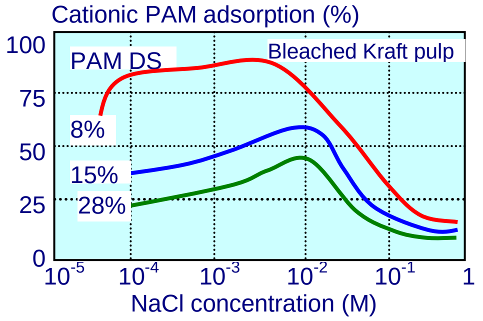
These are the most widely used conventional polymeric retention and drainage aids as they can be easily produced with a range of molecular weights and charge character. Polyacrylamide itself is essentially nonionic as can be seen from its formula at left and is rarely used as a retention aid in this form. However, acrylamide can be co-polymerised with other monomers or the polymer hydrolysed to produce a range of anionic polymers (such as when co-polymerised with acrylic acid) or cationic polymers (such as when polymerised with N, N, N-trimethylaminoethyl methacrylate as shown at right). The polyacrylamides used as retention aids are low-moderate charge polyelectrolytes of medium-high molecular mass (5-20M Daltons). Polyacrylamides are also used as dry strength additives, but their molecular weight is much lower (usually < 1M Daltons). They are widely available as powders or water-in-oil emulsions with a 25-50% solids content. Polyacrylamides can also be reacted with glyoxal to form derivatives used primarily as wet strength agents. The polyacrylates are also used in their own right as dispersants.



$$\left(\begin{array}{l} \quad CH_3 \\ \quad\ | \\ -CH_2-CH- \\ \quad\ | \\ \quad C=O \\ \quad\ | \\ \quad O \qquad Cl^- \end{array}\right)_n \begin{array}{l} \\ \\ \\ \\ \\ \\ \\ \ | \\ CH_2-CH_2-N^+(CH_3)_3 \end{array}$$

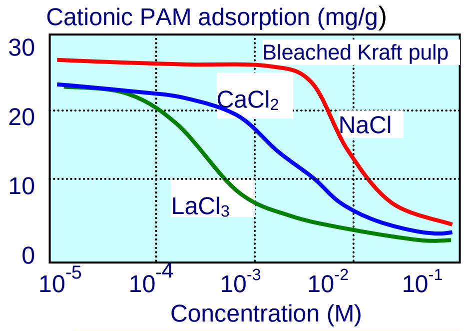
The charge character of polyacrylamides can be defined either in terms of the degree of substitution (DS), which is usually expressed on a molar basis as the % charged monomer content or by the actual charge, expressed as equivalents per unit mass. Cationic polyacrylamides contain 20-70% charged monomer units with an overall charge density of 1-4 meq/g. The charge character of most commercial cationic polyacrylamides is independent of pH, as the cationic monomers usually contain quaternary nitrogens (as shown in the example above). Anionic polyacrylamides cover a comparable charge range, but their charge becomes more negative as the pH is raised due to ionisation of the carboxyl groups (see the following examples of anionic polyacrylamides - here for improving fines and AKD size retention, here for its reflocculation abilities in a dual system with PEI and here for its use as a retention aid with TiO_2).

In their conventional form, polyacrylamides are linear polymer chains in which the molecular extension in solution is strongly influenced by the polymer's charge density and the solution's electrolyte content. The actual chain extension is considerably less than the theoretical length of the polyacrylamide chain, which, for a 10M Dalton polymer, would be about 40µm. The polyacrylamide's molecular mass affects its adsorption for the reasons given generally under polymer, but the particularly high chain length of polyacrylamides is important in terms of the surface accessibility factor. The illustration of this shows the substantial reduction in adsorption with increasing molecular mass up to 10M Daltons.



Source: Lindstrom and Wagberg,
Tappi J., 1988, 66, 83.

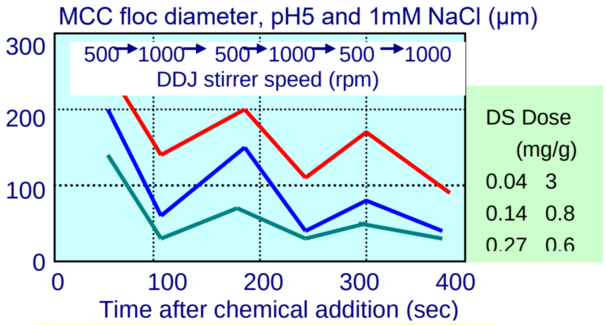
Because of their effect on polymer conformation, electrolytes have a significant impact on polyacrylamide adsorption as shown in two figures shown below. The first figure (at right) shows increasing initial adsorption as the NaCl concentration rises from a low level; this is caused by the shielding of the repulsion between cationic charges on the polymer chain, which leads to a less extended polymer conformation. Above a certain NaCl concentration, the attraction between the particle surface and the polymer is shielded leading to reduced adsorption. As would be expected for a charge-related effect, the magnitude of the changes in adsorption increase as the polyacrylamide becomes more cationic (higher DS).



Source: Pelton in J.Colloid Interface
Science, 1986, 111, 2, 215.

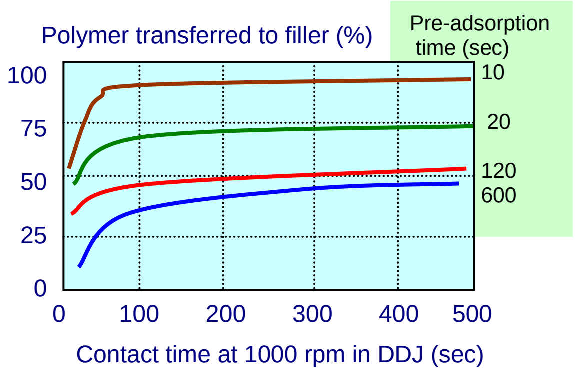
The second figure (at left) shows the significant difference between electrolytes containing cations of different valency. In this particular case, the increased electrolyte concentration reduces polyacrylamide adsorption due to increased shielding of polymer-fibre interactions and competition for adsorption sites between the cation and the polymer. The cation of most practical importance in papermaking is calcium. It is important to note from this illustration that polymer adsorption is particularly sensitive to calcium concentration in the range 20-100 mg Ca/l, ie the range covered by many mill waters.

Despite such effects, polyacrylamides have adequate molecular extension to function as bridging polymers under most papermaking conditions. As such, they generate stronger flocs than other single chemical treatments, but not as strong as those from dual component retention aid systems (see this figure). Despite these flocs being strong, they have limited ability to re-form (re-flocculate) once they are broken down at high shear.



Source: Swerin et al in J.Pulp Paper Science, 1997, 23, 8, 374-381.

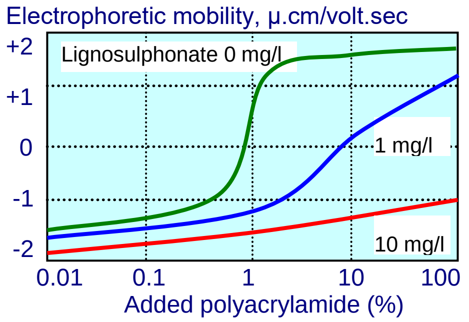
This is illustrated in the example shown here at right for three polyacrylamides of the same molecular mass (4M) but with varying cationicity (DS, degree of substitution). The dose of each polymer was double the level required to neutralise the negative surface change of the micro-crystalline cellulose (MCC), the original particles of which had a diameter of 22 μm and total charge of 10 μeq/g. The alternating high/low shear in the DDJ caused a progressive overall diminution in particle size, but with some recovery each time at the lower shear level. This effect is usually attributed to disruption of adsorption and re-distribution of the polymer into a flatter adsorbed conformation on the particle surface with reduced bridging potential. The floc size at any shear level decreases with increased charge density of the polymer and this is again attributed to the polymer adopting a flatter adsorbed conformation due to the greater charge attraction. The impact of the addition of a second component on reflocculation with a polyacrylamide is shown here for colloidal silica, here for bentonite and here for polyethyleneimine.



Source: Swerun and Odberg in "Fundamentals of Papermaking Materials" Proc. 11th FRS, Cambridge, 1997

The example at left also shows that the adsorption location/conformation of a polyacrylamide can change over time with prolonged contact. In this case, the polymer (dose 1 mg/g) was contacted with the fibre suspension (10 g/l) for times from 10 to 600 seconds before adding a relatively large concentration of calcium carbonate (5 g/l). As the pre-contact time increased, the amount of polyacrylamide transferred from the fibre to the filler surface decreased and the transfer rate was slower. These results were attributed to the ability of the polymer to penetrate more into the fibre's pores at longer pre-contact times and thus be less available for transfer than at shorter pre-contact times.

Like all cationic polymers, the performance of cationic polyacrylamides is adversely affected by anionic trash. As shown at right for micro-crystalline cellulose, very low levels of lignosulphonate can prevent the adsorption of the polymer, as indicated by the inability of the added cationic polymer to lower the negative surface charge at the higher lignosulphonate level. In such cases, anionic rather than cationic polyacrylamides may be the more effective, but a cationic substance would still normally be required to sensitise the fibre surface to adsorption of the anionic polymer, thus forming a quasi-dual component system.



Source: Lindstrom, Tappi J., 1974, 57, 12, 94.

In most applications as retention/drainage aids, conventional polyacrylamides are being used as part of multi-component systems, such as:

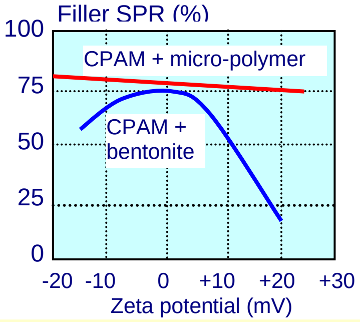
- with bentonite in Ciba's Hydrocol system
- with colloidal silica in variants of the original Compozil system from Eka Chemicals
- with other polymers like cationic starch or low molecular weight, highly cationic polymers such as PEI (see example of effect on water removal under pressing).

Such systems are widely used for many paper grades, even those with a high level of anionic trash in the furnish, provided that this is pre-neutralised first. With the exception of the approach adopted in the Hydrocol system, polyacrylamides are normally added just after the pressure screen and before the flowbox in order to avoid the higher upstream shear levels. The doses of polyacrylamides vary from as low as 0.1 up to about 1 kg/tonne paper. Doses for the lower molecular weight polyacrylamides used as dry strength additives are higher at 2-5 kg/tonne paper. High levels of dilution water are often used to lower the viscosity of the polymer solution and facilitate mixing with the papermaking stock and this aspect is discussed further under dosing.

The most recent development in polyacrylamide chemistry is the branched polymers (termed micro-polymers), which are being used in a similar manner to inorganic micro-particles such as bentonite and colloidal silica. These were originally developed by Cytec, but the products are now being developed further and marketed by Ciba. They are made by micro-emulsion technology from acrylic acid/acrylamide with bismethylene-acrylamide as a cross-linking agent to give an anionic product that has "particulate" character at its core, but with an outer layer of (anionic) polymer strands extending out into the bulk solution (referred to as a "corona" structure). An important variable is the level of cross-linking agent, which can give products with different core characteristics. The optimum molecular conformation aims to permit a greater range of interactions with the pre-added cationic or anionic polyacrylamide (the second component) because of the flexibility of the outer polymer strands (compared to the rigidity of inorganic micro-particles). From light-scattering data, the dimensions of the micro-polymers are 300-400nm as a hydrodynamic diameter with molecular masses from about 20M to >100M Daltons.

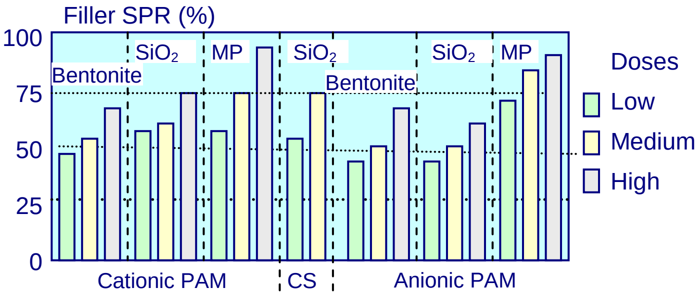
Initial development of these micro-polymers focused on improving the formation quality of filled fine papers, whilst maintaining an existing level of filler/fines retention and drainage, but current generation products now enhance all three parameters concurrently. Data from various machines give speed improvements (ie better drainage) of around 0.5-5% (depending on grammage), much better filler SPR (+10 to +30%) leading to less 2-sidedness plus formation improvements. The micro-polymer has also been shown to work well in the presence of cationic starch and be less sensitive to different starch chemistries than colloidal silica. Micro-polymer doses are around 0.2 kg/tonne and it was reported that micro-polymer technology was being used to make 5M tonne of paper world-wide in 1999.

Data from trial work comparing the micro-polymer with bentonite on a pilot paper machine is shown below for a 70:30 bleached hardwood/softwood Kraft furnish with added PCC and ASA size. The micro-polymer system was able to maintain high filler SPR (75-80%) even at 35% retained filler in the paper despite a substantial change in zeta potential (see figure at right). Formation quality of the paper was consistently better at the same drainage and retention levels for the micro-polymer system.



Source: Honig, D et al in Proceedings Tappi Papermakers Conference, 1999, 161-171.

Overall, the doses (around 0.15 kg/tonne for the micro-polymer) and system characteristics were claimed to be much more stable for the micro-polymer system.



This same study also compared the performance of various retention aid systems for a wood-free furnish at a 45% filler content using a DDJ (see diagram at left). It is evident that all systems gave reasonable performance, notably at the high end of their dose ranges, but that the micro-polmer (MP) gave the highest retentions when used with both anionic and cationic polyacrylamides. A normal colloidal silica system with cationic starch (CS) is included as a reference.

Polyacrylates

These are polymers of acrylic acid and are used in papermaking as dispersants, most commonly in the preparation of mineral pigments that are supplied in a slurry form. The use of dispersants enables the slurry to be prepared at a pumpable high solids content (eg 70%), which is essential in the production of coating formulations. The acrylic acid monomer is also used to prepare anionic polyacrylamides by co-polymerisation with acrylamide. Polyacrylates possess a very high anionic charge density (about 14 meq/g) under alkaline conditions, but this is lost at acid pH due to conversion to the unionised acid form. When these polymers are present at the wet end (due to the recycling of coated broke or sometimes due to the use of wet end fillers in a slurry form), the highly anionic polymer becomes part of the anionic trash fraction that interferes with the performance of cationic additives. As the polyacrylate dose may be up to about 0.4% on pigment, the anionic charge present corresponds to about 0.05 meq/g pigment solids which is comparable with the anionic charge content of bleached Kraft pulps.

Polyaluminium chlorides (PAC)

This form of aluminium compound, sometimes called polyaluminium hydroxychloride, has taken over from alum in some applications for sizing with rosin and is also used for neutralisation of anionic trash. Compared to alum, PAC has the advantage of being less acidic with a greater cationicity and more stable polymeric character. PACs are normally prepared by the controlled neutralisation of aluminium chloride with an alkali and, depending on the extent of neutralisation, this yields a product with the general formula:

$Al_n(OH)_mCl_{3n-m}$ where the basicity is defined as m/3n

The charge of the aluminium species produced increases with basicity, but the charge per Al atom decreases, an extreme example being the polymer $Al_{13}O_4(OH)_{24}(H_2O)_{24}^{7+}$. This is a highly charged complex in which the charge on the Al atom is only about +0.5 (compared to +3 in the chloride). These polymers can be relatively large molecules with chain lengths up to about 20nm. Sulphate ions are sometimes added to these products in order to lower their cationicity. It has generally been found that less cationic PACs of lower basicity (30-50%) are best for sizing with rosin, whilst the more cationic PACs of high basicity are best for charge neutralisation (see this example of the use of PAC for neutralisation of anionic trash). PACs are also used in papermaking systems with high electrolyte levels to aid the retention of anionic starch.

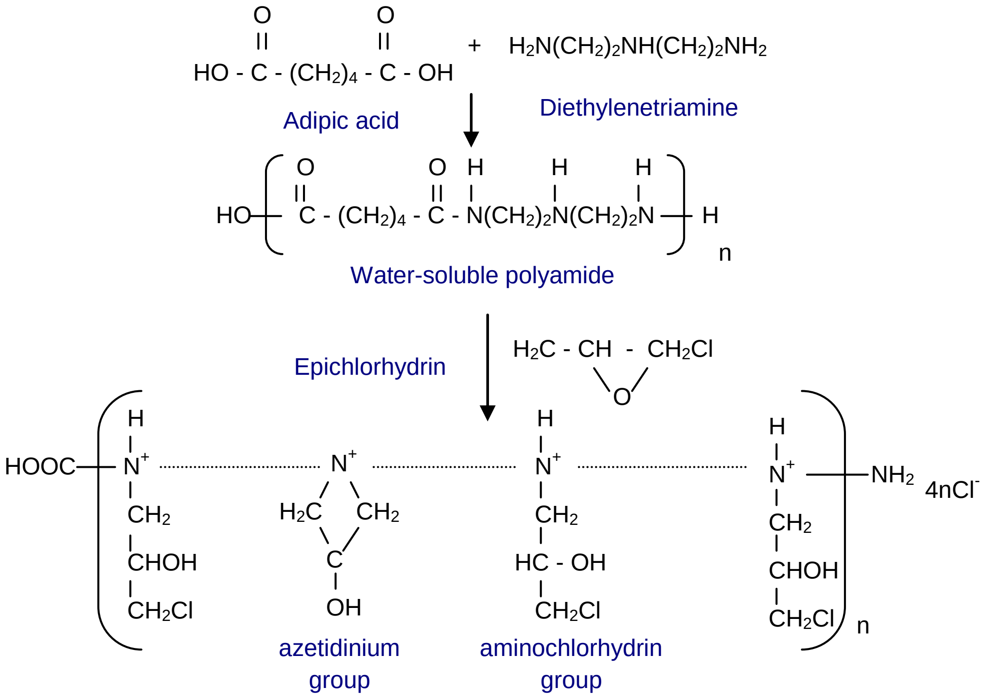
Polyaluminium silico-sulphate

This form of pre-polymerised aluminium compound was developed in Canada as an alternative to alum and PAC. It has some similarities with PAC in terms of more stable cationic character and low acidity and has the possible advantage of introducing no chloride ions into the process.

Polyaminoamide-epichlorhydrin (PAE) resins

These resins are used principally as wet strength agents, but, as moderately cationic chemicals, they have also been used as part of retention aid systems and as retention/cure promoters with AKD sizes. The key difference between these resins and the formaldehyde-based UF and MF resins is that they are effective at neutral pH conditions (pH > 6), a region where the formaldehyde-based resins have lost their curing ability. PAE resins can be used down to about pH 5 and this broad pH tolerance allied to acceptable cost-effectiveness has made them the most widely-used wet strength agent in papermaking today. On machines with a Yankee dryer, PAE resins also enhance adhesion to the cylinder, thus facilitating later creping and can also be used in their own right for this application.

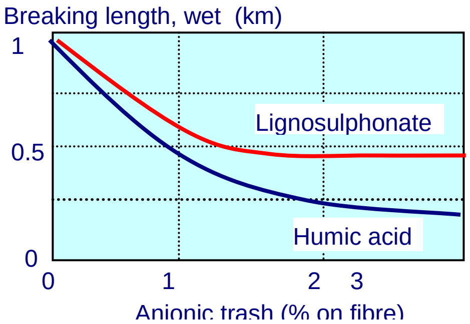
PAE resins are made from a dicarboxylic acid (such as adipic) and a triamine to yield an aminopolyamide, which then undergoes a series of reactions with epichlorhydrin to generate a partly-polymerised (B-stage) resin (see figure below). The B-stage resin is water-soluble and is moderately cationic due to the quaternary nitrogens in the azetidinium groups and the tertiary nitrogens in the unconverted aminochlorhydrin groups. The cationic charge density depends on the balance of these two units with a maximum value of about 9 meq/g PAE solids for aminochlorhydrin groups under acid conditions or for azetidinium groups at any pH. The azetidinium groups in the resin are the active components, which, at the elevated temperatures within the machine drying section, react with amino groups on other molecules to form a highly cross-linked structure (the C-stage resin) surrounding the fibres in the sheet. There is not thought to be any reaction between PAE resins and cellulose hydroxyls, but they can react, albeit slowly, with water to form non-reactive diols.



Despite some conflicting evidence, PAE resins do seem to have the potential to react with any available carboxyl groups to form an ester linkage via the azetidinium hydroxyl. This is certainly in line with practical observations where wet strength increases with a pulp's natural carboxyl content (ie higher with unbleached than bleached Kraft pulps) or where a pulp is firstly carboxymethylated. This ability to react with carboxyl groups is made practical use of in the application of carboxymethylcellulose (CMC) or other carboxyl-containing polymers (eg anionic polyacrylamides) with PAE resins, particularly where high doses are required to give maximum wet strength with bleached chemical pulps.

With such pulps, the adsorption of PAE resins is limited by the pulp's low anionicity, but the pre-addition of CMC reduces the resin's cationicity thus allowing more resin to be adsorbed before neutralising the pulp's charge. The optimum CMC dose depends on its anionic character, but is typically 50-100% of the PAE resin dose. The order of addition of CMC and resin does not appear to be critical. PAE resins alone have a small enhancing effect on dry strength, but their use with CMC allows a more significant increase in dry as well as wet strength. This use of CMC with PAE resins is akin to the use of cationic starches of lower cationicity as the starch dose is increased, as this option is not available for additives of fixed chemistry.

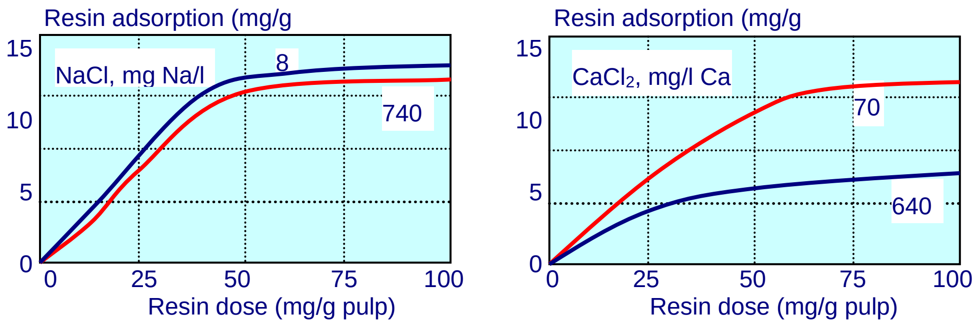
As with all water-soluble additives, the overall performance of PAE resins is dependent on their initial adsorption, which determines their single pass retention and then on converting the retained resin into an effective form for contributing wet strength. The factors affecting adsorption of PAE resins are similar to those for other cationic additives (eg cationic starch), but, as the PAE resins are substantially more cationic, they have an even stronger adsorption tendency, particularly on the fines fraction. Pulp refining can enhance resin efficiency by providing a greater surface area for adsorption, but this is only beneficial above a certain resin dose. Refining is often undesirable for some wet strength grades (due to adverse effects on softness and bulk) so this technique is not always available and resin adsorption has to rely on the natural fines in the pulp(s). For applications where low resin doses are possible (ie low wet strength specification in the paper), prior addition of a low molar mass cationic polymer can saturate the fines and neutralise any anionic interferants present, thus allowing the wet strength resin to be adsorbed on the well-retained fibre fraction.



Reference: Linhart "Wet strength resins" in Chapter 7 "Applications of wet end chemistry", Blackie, 1995.

Anionic trash is generally undesirable as it reduces the cationicity of the resin, but, as noted above for CMC addition, this can sometimes be beneficial to resin performance. In practice (at least for the dominant wet strength grades such as towel), anionic trash should be naturally low (in bleached Kraft pulps) or potentially low due to efficient upstream washing (with deinked pulps). The potential adverse effect of two forms of anionic trash are shown in the figure at left (although neither should be present at such levels on most machines using wet strength agents).

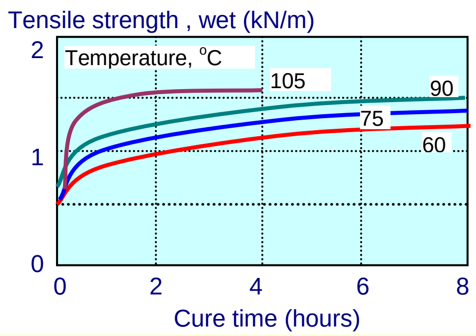
Dissolved electrolytes, particularly multi-valent cations, can also impair resin adsorption. In the data shown below, 27 g/m^2 handsheets were made with a PAE resin having a cationic charge density of about 3 meq/g resin solids. At low electrolyte levels, the maximum resin adsorption corresponded to the anionic (carboxyl) content of the bleached softwood Kraft pulp (35 meq/kg). Whereas the increased sodium chloride concentration has a neutral or marginally beneficial effect on adsorption of this PAE resin, the increase in calcium concentration impaired resin adsorption significantly. However, both salts had an adverse effect on paper wet strength and this was attributed to changes in the amount of resin exchanged with cations (which decreased at high electrolyte levels for both salts) as well as changes in the amount of total resin adsorbed. This change in calcium concentrations is quite typical of possible changes in real papermaking systems, but sodium concentrations are unlikely to change to this degree (see this example for UF resin). Alum would not normally be present in wet strength grades, but PAE resins can tolerate the normal levels used for sizing with rosin.



Reference: Ampulski and Neal in Nordic Pulp Paper J., 1989, 2, 155-163.

Once retained, the cure rate of PAE resins is slower than for UF/MF resins and is not influenced by pH over the normal range of pH 4-8, although resin adsorption does increase with raised pH (due to increased particulate charge). As shown in the figure below, sheet temperature has a significant influence on the cure of PAE resins, but on-machine cure is at best about 50% of the ultimate cure, which can take up to 2 weeks to achieve depending on storage temperature.

Once fully cured, recovered paper/broke containing PAE resins is very difficult to repulp due to the permanent nature of the wet strength effect. Fresh (ie not fully-cured) broke can be repulped with hot water (80^{o}C) or at high (pH > 11) with alkali (sodium hydroxide or carbonate). Aged (ie fully-cured) broke requires more stringent conditions, which has traditionally used sodium hypochlorite (1-2% on product) at slightly acid to neutral pH (6-7), but this has the (environmental) disadvantage of being chlorine-based. A non-chlorine (but more expensive) alternative is sodium monopersulphate. In view of the sensitivity of PAE resins to residual chlorine, the repulped broke should be treated before re-use with a reducing agent such as sodium sulphite to destroy any excess chlorine.



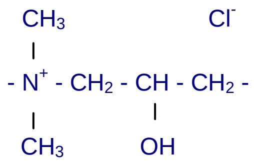
Reference: Thielez and Anderson in "Chemistry of Neutral Papermaking" Pira Conference , 1987.

Another reason for not using hypochlorite for broke repulping is the concern about producing organochlorine compounds. This concern also impacts on the resin itself, as, due to the presence of chlorhydrin groups, uncured PAE resins are determined as part of the organochlorine fraction in the standard test for AOX (adsorbable organo-halogens). The fully-cured resin eliminates the attached chlorine as inorganic chloride. Reaction of epichlorhydrin with the aminopolyamide also generates specific chlorinated compounds such as dichloropropanol (DCP) and chloropropanediol (CPD). Levels of these two undesirable chemicals in commercial resins were around 1% and 0.5% respectively during the 1980s (in products at 12.5% solids content), but have been progressively reduced since that time. Today, a range of PAE resins are commercially available containing less than 0.1% DCP+CPD and at best as low as 0.0001% (1 ppm) DCP and 0.0005% (5 ppm) CPD. The cleanest products are produced using a final bacteriological treatment which dechlorinates the residual chlorinated organics. The driving forces for these changes have been a combination of pressures on product labelling, concerns about occupational health and the need to reduce AOX levels in mill wastewaters and the organochlorine content of papers.

PAE resins are supplied at a solids content of 12.5-40% and have an acid pH (3-6) in order to minimise the ongoing polymerisation reactions. Addition rates are up to about 1% resin solids on pulp with the resin normally being added to the thick stock, sometimes after dilution to about 1% solids content in order to improve mixing and distribution. Where needed, CMC (or other anionic promoters) can be added either before or after the resin. Other anionic additives (eg dyes or brighteners) should be added well away from the resin addition point. Foam can sometimes be associated with use of PAE resins, particularly when used on rosin-sized grades, but this is usually caused by excessive use or poor adsorption/retention and should thus, at least in the first instance, be tackled at source rather than by addition of (more) foam control chemicals.

Polyamines

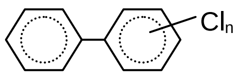
Polyamines are a generic group of polymers made by a condensation reaction between alkylamines (eg dimethylamine) and cross-linking agents such as epichlorhydrin. Monoalkylamines or ammonia can also be used to introduce some branching in the polymer chain. The resulting polymers have a moderate molecular weight (0.1-1M Daltons) and a high cationic charge density at all pH levels, the nitrogen atoms being predominantly quaternary as shown at right for a typical repeating unit. As the molecular mass of these polymers is not high, commercial products are usually available as solutions having a solids content of about 20-40%. Polyamines are used for charge neutralisation, so the doses are dictated by the cationic demand in the system, ranging up to about 2 kg/tonne paper.



$$-\underset{CH_3}{\overset{CH_3}{N^+}} - CH_2 - \underset{OH}{CH} - CH_2 - \qquad Cl^-$$

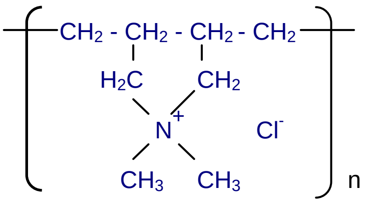
Polychlorinatedbiphenyls (PCBs)

These substances (formula at right) were used up to the 1970s as solvents in the coatings applied to carbonless-copy papers. This was stopped on environmental grounds in the early 1970s, but PCB residues at the ppm level can still be detected in mixed recovered papers.



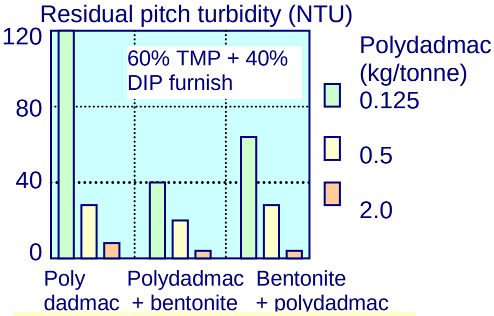
Polydiallyldimethylammonium chloride

Polydadmacs (general formula shown at right) are made by polymerising diallyldimethylammonium chloride. They have a similar molecular weight range to the polyamines and are also fully cationised over the whole pH range with a charge of about 6 meq/g. As the molecular weight of these polymers is not high (<1M Daltons), commercial products are usually available as solutions having a solids content of about 20-40%.



Polydadmacs have a number of applications in papermaking:

- for neutralisation of anionic trash, in which case the doses are dictated by the cationic demand in the system and can range up to about 2 kg/tonne paper (see example of this application here).
- as a drainage aid (see example here)
- for the control of pitch and stickies as a dual component system with bentonite, as shown in the example at right for pitch. It is evident that the post-addition of bentonite enhances the performance of the lowest polydadmac dose.



Source: Stockwell in Procedings Pira Filler Conference, Manchester, 1997.

Polydisperse

This is a term used in colloid chemistry to denote particles having a wide range of particle sizes, in contrast to monodisperse particles. All papermaking raw materials are polydisperse. It is also sometimes used in an analogous way in relation to the molecular weight range of polymers.

Polyelectrolyte

This is the name for polymers that possess a charge on the polymer backbone with associated counter ions of opposite charge. The counter ions tend to be small cations (Na^+) or anions (Cl^-), which contribute to the solution conductivity, but the charged polymer chains are too large and immobile for this. The term "polyelectrolyte titration" is synonymous with colloid titration. There are many polyelectrolytes used as paper additives in the two possible forms of anionic polyelectrolytes and cationic polyelectrolytes.

Polyethylene

This material (see formula at right) is not common in papermaking systems, except perhaps during stock preparation on machines making recycled grades (as part of the rejects). However, it is used for coating of photographic base papers, as a barrier coating for liquid packaging papers and in the form of a nonionic emulsion as a coating lubricant.

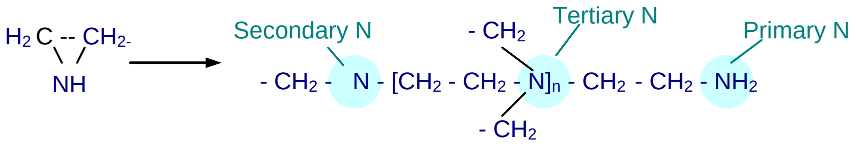
$- [CH_2 - CH_2]_n -$

Polyethyleneglycol

These chemicals are discussed under glycols.

Polyethyleneimine (PEI)

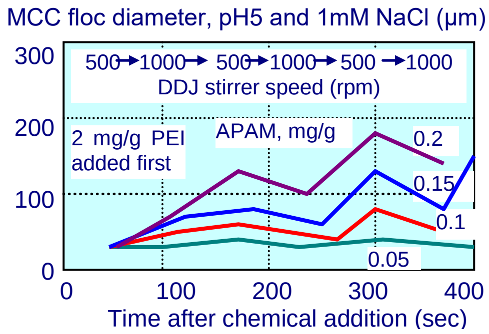
These polymers are probably the second most widely-used retention and drainage aids after polyacrylamides, but they also been used (although very little today) as a wet strength agent. Polyethyleneimines are manufactured from ethyleneimine (aziridine) by an acid-catalysed chain reaction. The resultant polymer has a branched structure containing about 25% primary, 50% secondary and 25% tertiary nitrogens as shown below in its nonionic form:

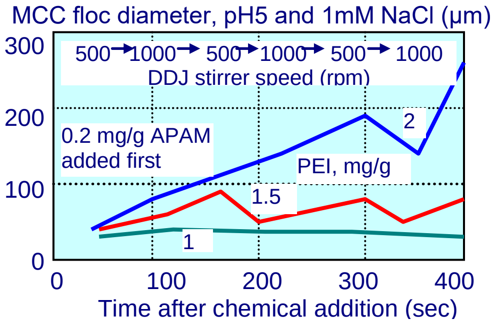


PEI has a high cationic charge density (about 23 meq/g) under acid conditions (pH 3) when all the nitrogens are protonated. As the pH is raised, the nitrogen atoms progressively lose their protons, commencing with the tertiary nitrogens and finally the primary nitrogens at about pH 9. Under alkaline conditions at about pH 10, PEI is effectively uncharged. Its maximum chain length is constrained by its branched structure, which could lead to gel formation at very high molecular masses, so commercial products are available up to only about 1M Daltons. PEI is a compact, spherical molecule with a solution diameter for a 600k molecular weight polymer of about 125 nm, increasing to about 600 nm on adsorption. Modified PEIs are available by co-polymerisation (eg with polyacrylamide) and cross-linking to extend their chain length, but this reduces their cationic charge. Commercially-available modified PEIs have a cationic charge density of about 6 meq/g. PEIs are sold as alkaline solutions containing 30-50% polymer. A somewhat similar chemistry is represented by the dendrimers based on polypropyleneimine.

The high charge and moderate molecular mass mean that PEI functions as a flocculant by a combination of charge neutralisation and patch attraction. As shown in this figure, the performance of PEI alone is adversely affected by shear, but its performance is much less affected by shear when it is combined with a second component such as a polyacrylamide. In one such full-scale example, the single pass filler retention in a mechanical pulp furnish increased from 38% with a cationic polyacrylamide dose of 0.3 kg/tonne to 47% when using a PEI dose of 0.6 kg/tonne with a much reduced polyacrylamide dose of 0.07 kg/tonne. An important characteristic of polymers functioning by a charge-patch mechanism is that, despite their relatively poor floc strength, the flocs do have the ability to reform (ie to reflocculate) once the high shear is reduced. This is illustrated in this example comparing PEI with polyacrylamide.

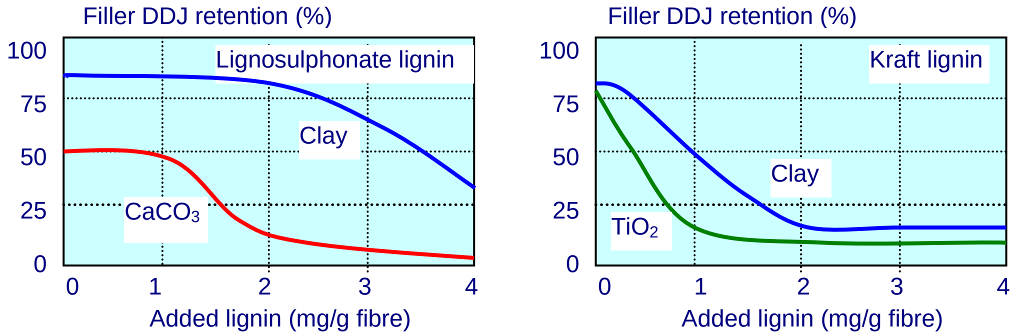
Data on the shear resistance and reflocculation ability of polyethyleneimine with an anionic polyacrylamide is shown in the two figures below for micro-crystalline cellulose (MCC) (see figure here for effect with various polyacrylamides on their own). The modified PEI had a cationic charge of 7 meq/g at pH 5 and the anionic polyacrylamide (molecular mass 3M Daltons) had a negative charge of about 2 meq/g (corresponding to a DS of 0.16). In this work, the shear is cycled between two levels by varying the impeller speed in a DDJ.





Source: Swerin et al in J.Pulp Paper Science, 1997, 23, 8, 374-381.

In the first experiment (left-hand figure), the PEI is added first, but little flocculation of the micro-crystalline cellulose (MCC) is achieved until the polyacrylamide dose exceeds 0.1 mg/g. From separate experiments, it was evident that the PEI at this dose was not fully adsorbed and that some of the interaction of the anionic polyacrylamide was with dissolved PEI and it is known that this polymer complex does have some flocculating ability. When the order of addition was reversed (right-hand figure above), a high level of flocculation is still achieved, but quite a high dose of PEI (above 1 mg/g) is required. These graphs are quite different in shape to those for a cationic polyacrylamide with colloidal silica (see here) or with bentonite (see here). The progressive improvement in flocculation suggests some sort of sequential reconformation of the interacting polymers that leads to improved bridging.



Source: Pelton in Paperi ja Puuu, 1987, 3, 23-233.

As a highly cationic polymer, PEI has a strong interaction with anionic trash, leading to some loss of performance as the level of such substances increases. This is illustrated above for a mechanical pulp furnish at a PEI dose of 0.5 kg/tonne fibre. However, this interaction is potentially beneficial as it would allow other cationic additives to function more effectively. The performance of PEI is also susceptible to the presence of residual silicate in deinked pulps (see this example for a newsprint furnish). PEI can be used in this charge neutralising role as well as a patch-type flocculant. Modified PEI can also be an effective treatment for white pitch, as shown in this example. The ability of PEI to enhance water removal during both the drainage and pressing stages is shown here. The doses of PEI depend on the system chemistry, particularly the level of anionic trash, but would not normally exceed about 1 kg/tonne paper.

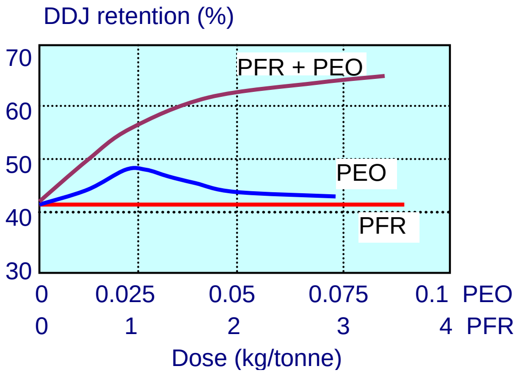
Polyethyleneoxide (PEO)

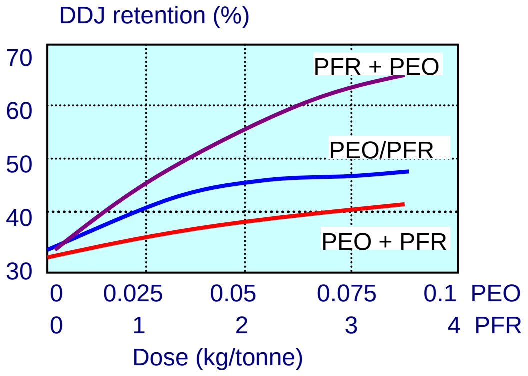
These are nonionic polymers of high molecular weight (5-7M for the grades used as retention aids) with a simple linear structure of (- O - CH_2 - CH_2 -) repeating units. When uncoiled, the chain length can extend to about 50µm. Despite their nonionic charge, they can still interact with surfaces through hydrogen bonds or van der Waals forces. PEO and polyethylene glycol (PEG) are synonymous names, the only difference being that PEG seems to be used for the lower molecular mass liquid products whilst PEO is used for the high molecular weight solids.

The original use of PEO as a retention aid was for wood-containing papers, notably newsprint mills, which often have difficulty in using cationic polyelectrolytes due to the presence of anionic trash. More recently, PEO has begun to be used at mills using recovered paper and the use of so-called “comb” co-polymers of PEO with polyacrylamide has begun to be explored. PEO is available commercially only in solid form as the solutions are both very viscous and prone to degradation.

PEO can be effective alone, but only in the presence of materials that are naturally present in some pulps, eg modified lignins. If these materials are not present naturally, they have to be added as a so-called co-factor, the most common being phenol-formaldehyde resin. The interaction between fibre, the PEO and the resin or lignin appears to be via hydrogen bonds between the PEO oxygen and the phenolic and cellulosic hydroxyl groups to form a complex 3-dimensional network.

The figures below show some results for PEO systems with a thermomechanical pulp using a dynamic drainage jar. The figure at left indicates that neither PEO or the resin has any affect on their own and the figure at right indicates that it is essential to add the resin prior to the PEO for the best performance.





Reference: Appita J., 1990, 43, 2, 125-129.

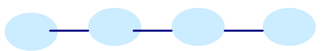
Polyisocyanates

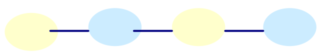
These chemicals are a fairly recent development for use as wet strength agents.

Polymers

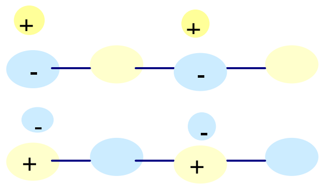
These are chemicals that consist of a long chain of units linked by covalent bonds. They can be classified in terms of various attributes of the polymer chain:

- ❑ repeatability of the monomer units, there being two types:
  - polymers with same repeating unit (homo-polymers) like cellulose or polyacrylamide
  - polymers with different repeating units (hetero-polymers) like cationic polyacrylamide and most hemi-celluloses

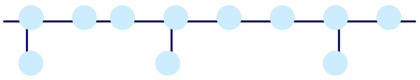


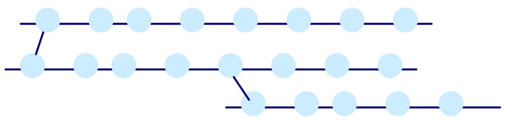


- ❑ the charge character of the chain, there being four types:
  - nonionic polymers such as polyacrylamide and polyethyleneoxide
  - anionic polymers such as CMC and the anionic forms of polyacrylamide and starch
  - cationic polymers such as polyethyleneimine, polydadmacs, polyamines, etc
  - amphoteric polymers with both anionic and cationic groups such as cationised potato starch.



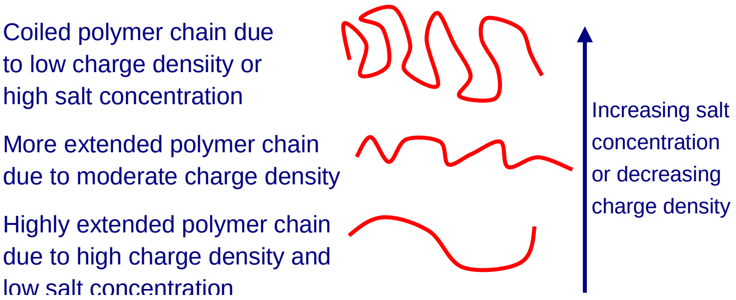
- ❑ the structure of the polymer chains, there being two main types:
  - linear polymers such as the amylose fraction of starch or conventional polyacrylamides
  - branched polymers, but with different levels of branching such as the simple pendant structures (comb polymers) exemplified by some of the natural polymers (glucuronoxylans, arabinoglucuronoxylans, guar gum), the multiple branching in polymers such as the amylopectin starch fraction and polyethyleneimine) and the tree-like branching in the dendrimers.





- the basic type of chemistry, there being two main sorts:
  - organic polymers, as listed above in their great variety of types
  - inorganic polymers, which are much smaller in number, the main examples in papermaking being the various aluminium-based polymers and zirconium chemicals.
- their degree of water-solubility, there being two sorts:
  - water-soluble polymers, which are the most common type added at the wet end and include the important hemi-cellulose fraction of wood/pulp
  - water-insoluble polymers, which includes arguably the most important substance in papermaking (cellulose itself), other wood/pulp components such as lignin and surface additives such as coating latices.

The behaviour of water-soluble polymers in aqueous solution is complex and not fully understood. Once dissolved (a process that is not always easy), the conformation of the polymers chains is highly variable and dependent on a number of factors. The chains are flexible due to rotation about carbon-carbon and other bonds and due to the influence of thermal energy on individual segments of the polymer chain. The whole molecule is continually changing its conformation in a fairly random manner. An important variable is the relative interaction between the polymer and water and between segments of the polymer chain. A decrease in water solubility (eg by reducing the temperature) leads to a more coiled, compact conformation ultimately leading to precipitation. The most common parameter for expressing the polymer size is its radius of gyration.

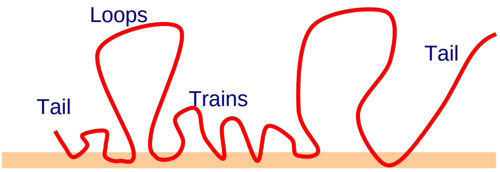


When polymers contain charged groups (like most polymers used in papermaking), the flexibility of the chain is reduced and a more extended conformation is adopted due to the repulsion between charged units along the polymer chain (see figure at right). However, the presence of dissolved electrolytes leads to a more coiled conformation due to shielding of the repulsion between the charged groups.

When a polymer is added to a papermaking furnish, it can do one of three things:

- remain unadsorbed in solution,
- become adsorbed on the particle surface or
- react with other dissolved materials such as polymers of opposite charge.

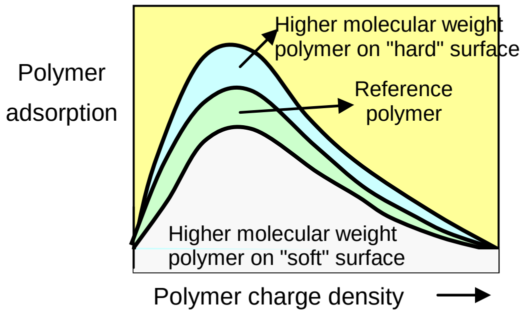
Any polymer deliberately added to the wet end is usually intended to be retained in the paper and therefore must be effectively adsorbed on particle surfaces. Due to its chain length and/or charge characteristics, it is likely that the adsorbed polymer will affect the state of particle aggregation although this may (eg retention aids) or may not (eg wet strength resins) be the intention. The mode of polymer adsorption on the particle surface dictates the type of aggregation that may be achieved. This adsorption mode is dependent on the concentrations and physico-chemical characteristics of the polymer and the surface and on the hydrodynamic conditions during mixing. Each polymer molecule has a large number of



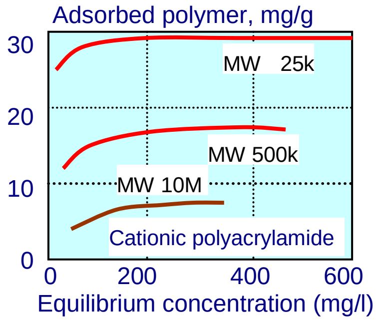
potential adsorption points on the particle surface leading to the "loop and train" adsorption patterns shown at right. The mechanism of the particle-polymer interaction can be electrostatic, hydrophobic or hydrogen bonding.

The adsorption process starts from a point of single contact and then proceeds to establish further contact points with the final outcome being determined by the attraction between the particle and the surface under the particular mixing conditions employed. Generally, the polymer conformation becomes flatter over time with fewer loops and more trains. This effect has been demonstrated for the case of a low cationicity polyacrylamide, where less than 10% of the cationic groups were initially bound to the fibre surface, but this increased to 80% after further mixing for 1 hour. By contrast, the adsorption of a lower molecular weight, more highly-cationic polymer changed little with time, reflecting the much stronger initial electrostatic attraction between this polymer and the negative surface.

The extent of polymer adsorption on a defined surface is determined by its molecular mass and the strength of attraction between the polymer and the surface, ie in the case of a charged polymer, largely by its charge density (see illustration at right). For a particular substrate and polymer type, the polymer has an optimum charge density for maximum adsorption. Initially, adsorption increases with polymer charge density due to increased electrostatic attraction, but, above a certain charge density, electrostatic repulsion between charged groups on the polymer leads to an expanded polymer volume, which lowers its adsorption.



The effect of polymer molecular mass is less easily predictable as it depends on the accessibility of the substrate's surface to the polymer. For a "hard" surface such as that of most mineral fillers (eg one having no internal voids or pores), adsorption tends to increase with molecular weight (notably at low charge densities) due to the increased size of loops and, with less hydrophilic polymers, due to decreased water solubility. However, in the case of a "soft" surface such as cellulose (eg one that does have internal voids or pores), the internal fibre surfaces can only be accessed by low molecular weight polymers, leading to a reduction in adsorption with increasing molecular weight (see illustration at left for a cationic polyacrylamide on a bleached chemical pulp).



Source: Wagberg in Nordic Pulp Paper Research J, 2000, 15, 5, 586-597.

Because adsorbed polymers change the surface properties of the particle, the state of aggregation of the particulate material usually changes. Polymer adsorption can lead to particle aggregation by one of two possible mechanisms - inter-particle bridging or patch attraction, although more complex mechanisms may be operative when other materials are present, eg as part of multi-component retention aid systems.

In real papermaking systems, it is often difficult to be precise about the prevailing aggregation mechanism due to the range of materials present, some well characterised and some not. Materials added for purposes other than aggregation (eg wet strength resins, which are normally low molecular weight cationic polymers) play a part in determining the extent of particle aggregation and influence the selection of any retention aid polymer (particularly its charge characteristics) added later. Polymers may also be deliberately used in combination to harness different flocculation mechanisms at the same time, eg the addition of a charge-neutralising or patch-type polymer such as polyethyleneimine followed by a bridging polyacrylamide or the various micro-particle systems.

Although added polymers are intended to adsorb on the particulate substrate, they may be prevented from doing so by interactions with other substances (usually other polymers) in solution. This type of interaction is discussed under anionic trash. This polymer-polymer interaction is similar to that used in the measurement technique variously known as polyelectrolyte titration, polymer titration or colloid titration, which is used to quantify the charge density of polymers or certain types of charges in the papermaking system.

Polypropyleneglycol

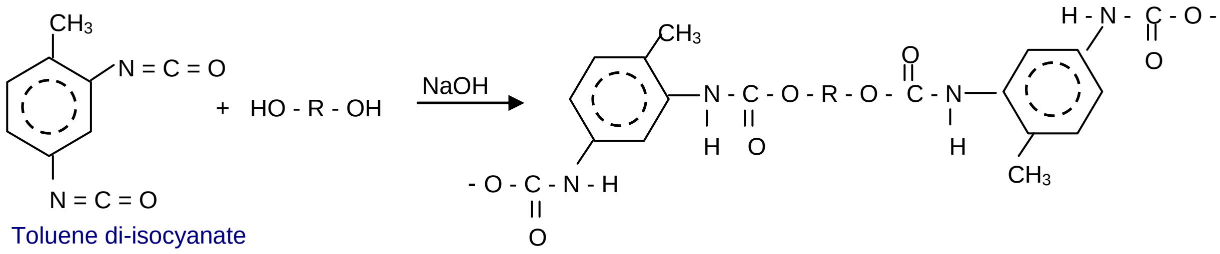
These chemicals are discussed under glycols.

Polysaccharides

These are carbohydrates that give a large number of monosaccharide units on hydrolysis, the most important polysaccharides in papermaking being cellulose, the hemi-celluoses and starches. Polysaccharides are also present in bacteria as an extra-cellular polymer, which allows them to form microbial flocs and slime deposits.

Polyurethanes

These polymers are mainly used for surface sizing, although they can be used at the wet end. Their chemistry is based on the reaction between a di-alcohol (glycol) and a di-isocyanate, as shown below.

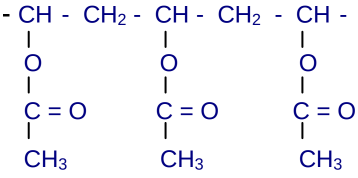


Toluene di-isocyanate

The di-alcohol could be glycerine mono-stearate, the long alkyl chain conferring considerable hydrophobic character on the molecule. Anionic or cationic chain extenders introduce carboxyl or positively-charged nitrogen groups into the polymer chain to give the optimum charge to suit different size press conditions (pH, electrolyte levels, charge balances and compatibility with other chemicals). Polyurethane sizes are supplied as colloidal dispersions with a particle size around 10 nm. Full sizing requires the hydrophobic groups to orient themselves away from the paper surface and this takes place at the elevated temperatures in the dryers following the size press.

Polyvinyl acetate (PVAc)

These homo-polymers (formula at right) are a type of latex used as coating binders and also as adhesives in the conversion of paper products. They are made by emulsion polymerisation of vinyl acetate and can also be produced as co-polymers with vinyl esters and unsaturated carboxylic acids. They are particularly

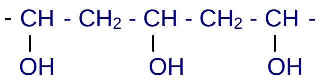


$$\begin{array}{lllll} -\,CH\,- & CH_2\,- & CH\,- & CH_2\,- & CH\,- \\ \;\;| & & \;\;| & & \;\;| \\ \;\;O & & \;\;O & & \;\;O \\ \;\;| & & \;\;| & & \;\;| \\ \;\;C = O & & \;\;C = O & & \;\;C = O \\ \;\;| & & \;\;| & & \;\;| \\ \;\;CH_3 & & \;\;CH_3 & & \;\;CH_3 \end{array}$$

useful for giving open, porous coatings with excellent resistance to blistering, but at the expense of lower binding power compared to SB or SA latices. Due to some hydrolysis to PVOH, they can interact via hydrogen bonds with clay surfaces and therefore affect the viscosity of coating mixes more than SA/SB latices. It has been found that co-polymerisation with ethylene maintains the high porosity, but also enhances the binding power. These binders are mainly used in the coating of packaging boards due to their good glueability with water-based adhesives.

Polyvinyl alcohol (PVOH)

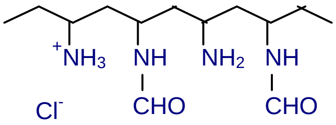
This chemical (formula at right) is made by complete or partial hydrolysis of polyvinyl acetate. It is an excellent film-former for use at the size press and binder for use in paper coatings, but application is often limited by its high price. For this reason, it is rarely used alone to carry out a certain function, but is used as a partial replacement for size press additives (mainly starch) and coating binders (starches and latices) that, although cheaper, are less effective per unit mass added. Binding strength and film formation improve with increased molecular mass and hydrolysis level, but water sensitivity is also greater when hydrolysis is complete. It is widely used with silica pigments as a special surface treatment for ink-jet printing papers and is also an excellent carrier for fluorescent brighteners. In tissue production, it is used as a creping adhesive by spraying onto the Yankee cylinder.



$$-\underset{\displaystyle OH}{\underset{|}{CH}} - CH_2 - \underset{\displaystyle OH}{\underset{|}{CH}} - CH_2 - \underset{\displaystyle OH}{\underset{|}{CH}} -$$

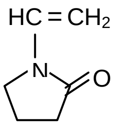
Polyvinylamines

polyvinylamines are made by the polymerisation of vinylformamide to give a range of polymers with molecular masses from 30k to 5M Daltons. This nonionic polymer is then partially hydrolysed to give polyvinylamines of varying degrees of cationicity up to a maximum of about 15 meq/g (see formula at right for an indication of the structures involved). As the nitrogen in the amine group is not quaternary, the actual polymer charge density is influenced by the pH as well as by the degree of hydrolysis. Because of this range of chain length and charge density, polyvinylamines could function as retention aids (high molecular mass, low charge) or charge-neutralising agents for anionic trash (low molecular mass, high charge).



Polvinylpyrrolidone

This polymer (formula of monomer at right) is used as a coating plasticiser and has been tested for its ability to stop brightness reversion in mechanical pulps.



Porosity

This term has two quite different meanings in papermaking:

- the porosity of papers (sometimes also called permeability) refers to the ease of passage of a gas or liquid through the sheet and is an important characteristic for grades such as filter papers and cigarette papers.
- the porosity of fibres usually refers to the ability of soluble macro-molecules to penetrate into the pores of the cellulosic matrix (see accessibility), which is dependent on the size of both the penetrating molecules and the pores themselves, the latter being largely determined by the extent of fibre swelling.

As well as being relevant to the end-use properties of some papers, the porosity of the paper web is also relevant to the penetration of surface-applied materials into the base sheet. Porosity is usually measured by the same equipment used to measure paper smoothness (eg Bendtsen, Gurley testers), but with the backing layer (that prevents air passing through the paper) removed.

Paper porosity depends on the particle size distribution of the sheet components and how they are arranged in the sheet. As fine particles fill in the gaps between fibres, the addition of fillers and the refining of pulps both have a negative effect on porosity. Sealing the paper surface chemically by adding a film-forming chemical such as starch at the size press closes off the paper pores, thus restricting ingress of any material. Any process that consolidates the sheet structure in the z-direction (eg pressing and calendering) increases its density and also reduces sheet porosity.

Potassium

Potassium (K, atomic mass 39) is a common alkali metal, but features in very few papermaking materials. It is also not very common in most fresh waters, so has little significance for papermaking.

Potassium monopersulphate

This chemical has been introduced as a chlorine-free replacement for sodium hypochlorite in the treatment of wet strength papers.

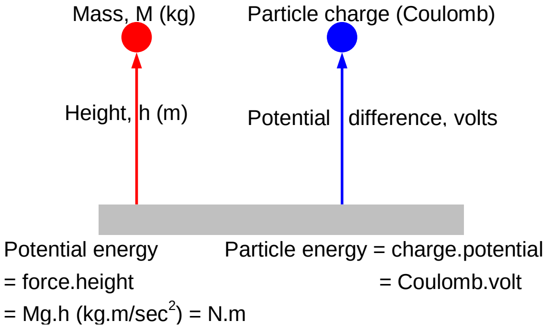
Potato starches

These are sometimes called farina and are one of the most common types of starch used in papermaking. They have a higher amylopectin content than wheat or maize/corn starches, virtually no fatty material and a low level of phosphate groups (see this table for comparison with other starch types). Their granules are the largest of all starches with a mass average of about 50 µm and are oval in shape. Potato starch is the only starch with phosphate groups covalently bound to the starch, in fact just to the amylopectin molecules, in the form of a phosphate ester through the hydroxyl on carbon 6 as $-H_2C-O-PO_3H_2$. This corresponds to a degree of substitution of about 0.004 with the counter ions being sodium, potassium, calcium and magnesium. The phosphate groups give potato starches a natural weakly anionic character (about 0.025 meq/g at neutral pH), which is responsible for their rapid swelling/hydration, lower gel temperature and higher viscosity compared to other starches.

Potential

In papermaking, this term is mainly used in the context of the electrical potential on a particle surface, as measured most commonly by its zeta potential. Electric potential at a certain point is measured in volts and can be considered to be the work done when a unit charge is brought from infinity to that point. Measurement of electrical potential (via a pH electrode) is used as an end-point in potentiometric titrations, which are used in papermaking as one of several possible techniques of charge titration.

The difference between potential and charge is important in relation to the two ways in which the presence of charged groups on a particle surface is quantified - either by direct electrokinetic measurement as a potential or by charge titration. This difference is highlighted in the figure at right, which uses the analogy between mass/height and



charge/potential. The particle charge is analogous to particle mass and is directly measurable in the titration technique as the quantity of electricity (in Coulombs or charge equivalents). The potential measured in the electrokinetic methods is analogous to the height above some datum (level). The energy of the charged particle is obtained from both the charge and potential and is analogous to the measurement of potential energy from mass x height. The difference between these two systems is that the surface potential of a particle is dependent on the charge density, as discussed here. Potential is an intensive property of the system, whilst charge is an extensive property.

ppmv

This is an abbreviation for parts per million by volume applicable to atmospheric gases.

Precipitation

This occurs when a substance (the solute) becomes insoluble in its solvent. It is mainly relevant in papermaking systems to inorganic electrolytes, the one exception being the precipitates formed when anionic trash interacts with added cationic polymers. The precipitation of an inorganic electrolyte occurs when the concentrations of the ions involved exceeds their solubility product. This can happen for a variety of reasons, which tend to be substance-specific, but this could involve a change in temperature or pressure in addition to changes in the concentration of component ions.

Such reactions in the bulk of the wet end stock or whitewater may not cause any specific problems provided that the precipitate remains within the bulk liquid phase as it will then be retained with the product or discharged in the machine wastewater. Problems arise if precipitation takes place (as they often do) on a nucleating surface such as a pipe or tank in the form of an attached scale. There is one deliberate precipitation reaction at some paper mills and this is the production of precipitated calcium carbonate, but this does, of course, take place outside the wet end in a managed chemical reactor.

There are many inorganic substances that may precipitate in papermaking:

- calcium carbonate
  This is the most common precipitate, which is usually formed by the instability of dissolved calcium bicarbonate. It may occur as a scale within shower systems or other applications where the fresh water is heated (eg starch cookers).
- calcium sulphate
  This is not a common precipitate due to its moderate solubility (about 2 g/l), but it can occur on machines with substantially-closed water systems with high sulphate addition from alum or sulphuric acid. Calcium sulphate in the form of gypsum is also used as a filler and coating pigment.
- calcium oxalate,
  This is not common in papermaking unless sulphite pulps are used.
- calcium silicate
  This may occur when silicates are used in deinking or bleaching and carried forward to the paper machine.
- calcium salts of carboxylic acids
  This is a particular problem for the resin acids in rosin as it converts them into an ineffective form and for colloidal pitch in virgin pulps, which is destabilised.
- aluminium hydroxide

This is common when alum is used at neutral pH, but becomes a problem only when it forms a hard, adherent scale. This tends to happen at higher process temperatures (+40°C).

- barium sulphate

  This is a more common occurrence at pulp mills due to the natural barium content of wood (higher in hardwoods than softwoods).

The prevention of precipitation reactions is mainly important in relation to the prevention of adherent scales and is thus discussed under that heading.

Precipitated calcium carbonate (PCC)

PCC is a synthetic form of calcium carbonate, which is manufactured from calcined natural carbonates by re-carbonation under controlled conditions. This gives a range of fillers and coating pigments with tailored morphology and surface chemistry.

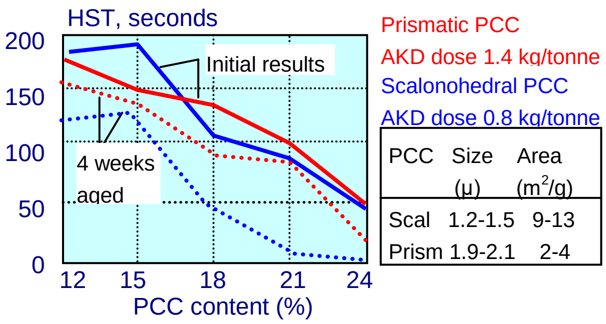
$$CaCO_3 \rightarrow CO_2 + CaO \quad \overset{\text{Transport}}{\text{to mill}} \quad CaO + CO_2 \rightarrow CaCO_3$$

The recarbonation reaction can be carried out near the site of limestone extraction or at so-called satellite plants near the user paper mill(s). In the latter case, the carbon dioxide for carbonation would probably be supplied in the form of flue gas from the mill's boiler plant. The main forms of PCC manufactured in this way are:

- rosette-shaped aggregates of calcitic, scalanohedral PCC particles, the normal wet end filler form which gives good opacity and brightness, whilst minimising adverse effects on bulk
- barrel-shaped particles of calcitic, prismatic PCC, which gives reasonable opacity, but with less adverse effect on paper strength. This form can be clustered to give reduced size demand.
- cube-shaped particles of calcitic, rhombohedral PCC, which gives enhanced opacity over scalanohedral PCC.

The particle size distribution of PCCs can be controlled during precipitation, but all tend to have a narrower distribution than natural carbonates. PCCs can be blended together to give intermediate effects and all types (including natural carbonates) can be pre-treated so that they may be used under acid conditions, usually referred to as acid-tolerant grades. The latter is particularly valuable for filler use in wood-containing papers, which, although not sized, suffer from loss of brightness under neutral/alkaline conditions.

All fillers increase the demand for sizing chemicals and this is particularly true for the most commonly-used filler PCC, the scalanohedral grade. This is shown in the figure at right, where the sizing at a fixed AKD dose declines with increased PCC content. The size demand to give about the same HST value for the lower surface area prismatic grade is about 60% of that for the scalonehedral grade.



PCC	Size (μ)	Area (m^2/g)
Scal	1.2-1.5	9-13
Prism	1.9-2.1	2-4

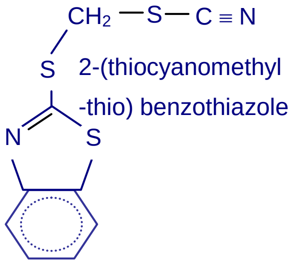
Source: Ozment in Proceedings 1994 Tappi Confererence, 169-172.

This set of data also demonstrates one of the further key issues for PCC-filled papers, which is the loss of sizing (size reversion) that is sometimes observed over time. In this particular case, the loss is substantial for the scalonehedral PCC, but much less for the prismatic PCC. Various mechanisms have been proposed for the observed effect; these range from a purely physical re-distribution effect in which the AKD changes its surface conformation or migrates into the PCC interstices to chemical effects attributed to hydrolysis of AKD caused by latent alkalinity within the PCC particle.

Preservatives

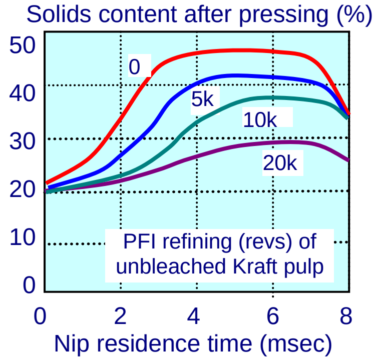
These are biocides that are added to the papermaking system in order to be retained in the product and thus stop the growth of micro-organisms (notably fungi) during later handling and use, eg in soap-wrap papers, label papers and wall-papers. Preservatives are best added to the paper surface (eg size press or coater) due to their poor retention when added at the wet end, but biocides are often needed in size press/coater formulations in any case to stop microbial problems within the circulation system.

Typical preservatives include organo-sulphur compounds such as benzisothiazolones (see example of TCMTB at right), dithiocarbamates and copper-8-hydroxyquinolinate. Chlorinated phenolics such as PCP have been discontinued for this application.



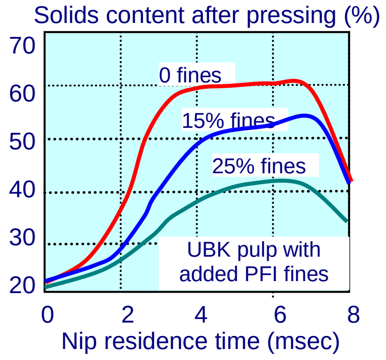
2-(thiocyanomethyl -thio) benzothiazole

Pressing



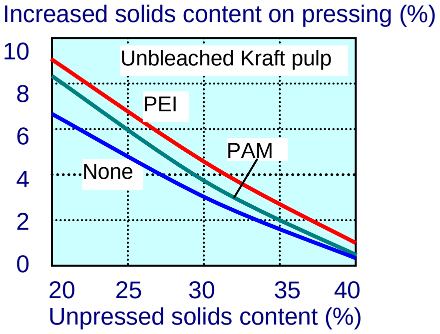
Source: Springer in Tappi J., 1991, 74, 4, 221-228.

This is the second stage of the overall process of removing water from the paper web. After the drainage stage, the sheet has a solids contents of 15-22%, which increases on pressing to 40-55%. Pressing involves the removal of residual unbound water, which, as in the wire section, is influenced by the particulate structure in terms of porosity and ease of water flow. As shown in the figure at right for different refining times (revolutions) in a PFI mill, increased refining tends to impair water removal in pressing and this has been shown to be partly due to the production of fibrillated surfaces. However, the fines generated on refining make the bigger contribution to the poorer pressability, as shown in the figure below at left for the same unbleached Kraft pulp.

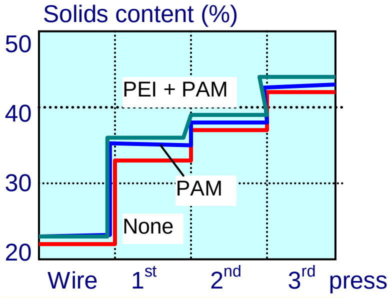


In view of this effect, it would be expected that the addition of drainage aids would have a significant impact on water removal during pressing, but this is not always the case. In the same study as quoted above (using the water retention value as in index of pressability), the best results (with cationic polymers) lowered the WRV by about 10%. The few other studies in this area have generally corroborated the beneficial effect of retention/drainage aid chemicals on pressing with some furnishes, but not with others.

The first example (below at left) shows quite substantial improvements on treatment with both a polyacrylamide (PAM) and polyethyleneimine (PEI) on an unbleached Kraft pulp, particularly when the pre-press solids content is at the normal machine level (about 20%). However, on pulps with easier natural water removal characteristics (eg bleached chemical pulps), chemical treatment had no effect on pressability and could, at high doses, have an adverse effect. Two possible mechanisms for the efficacy of the additives were postulated in this study - a reduction in migration of fines towards one side of the paper due to the improved fines aggregation and a reduction in the surface area of the pulps. Evidence for the latter was consistent across a number of samples, but the migration of fines was reduced both in cases when the added chemicals were effective and when they were not (see this example of the change in fines distribution with pressing).



Source: Stratton in Proceedings Paperrmakers Conference 1982,



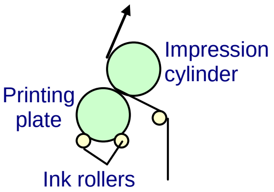
Source: Pelletier in Pulp Paper, 1997, December, 85-89.

The second example (see figure above at right) investigated the same two types of chemicals as above, but in this case across three separate stages of pressing. Although the polyacrylamide alone (dose 0.6 kg/tonne) was effective in promoting water removal, its combination (at a lower dose of 0.1 kg/tonne) with polyethyleneimine (dose 0.6 kg/tonne) gave the best performance. This was attributed to the smaller floc size with the dual polymer treatment, which is a common feature of such systems.

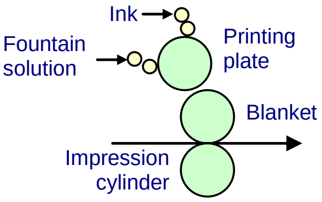
Printing

Many papers are used for printing and there are many types of printing process, detailed coverage of which is outside the scope of this document. In summary, the main printing processes are:

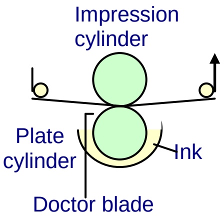
- letterpress, where the oil-based ink is applied to the raised surfaces on the printing plate. When this is pressed against the paper, the raised image is transferred to the paper. It is typically used for printing newspapers and some magazines. Letterpress inks dry by absorption or evaporation.



- lithography, where the oil-based ink is applied to the oil-receptive image areas of the flat printing plate, but the rest of the plate is made oil-repellent (water-receptive). As this is normally done via an intermediate blanket-covered roll, the usual term for this process is offset-lithography or just offset-litho. The fountain solution is an aqueous solution of chemicals that dampen the non-image areas of the plate and contains several chemicals to carry out different roles - surfactants for wetting, pH buffers, protective film-forming gums, emulsifiers, lubricants, and iso-propyl alcohol. Lithographic inks use water-resistant vehicles that do not bleed in water or alcohol and are typically an alkyd resin in a drying oil (eg linseed). UV-curing inks are also used. Lithography is used either for web or sheet printing of "glossy" magazines and books.



- gravure or rotogravure, where the ink is applied to recessed surfaces on the printing plate by immersion in an ink bath with excess ink being removed by a doctor blade. The impression cylinder is covered



with a resilient rubber covering. Gravure inks dry by heat-aided evaporation and comprise synthetic resins in a hydrocarbon solvent vehicle or a water/alcohol solvent mixture. Gravure is used for printing newspaper supplements, cartons and wrappers.

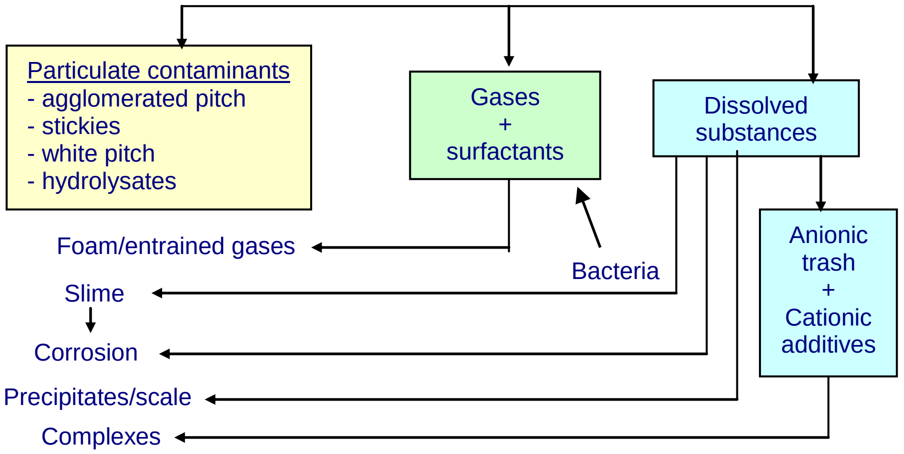
- flexography (or just flexo) is a modified letterpress process, where the printing plates are softer with less impact on the paper surface. Flexo inks are similar to gravure inks where the vehicle is an alcohol/water mixture which dries rapidly by evaporation and absorption.
- Xerography (photocopying), where a latent image is formed on a photo-conductive surface and transferred to paper by the attraction of oppositely-charged ink particles. The ink or toner particles are a suspension of black or coloured pigment in a thermo-setting resin (such as styrene-acrylate co-polymers), which dries (sets) by the application of heat.
- ink-jet printing, which is used for office printing rather than bulk commercial printing. A jet of ink is broken into droplets and the placement on the paper is controlled electronically. The inks used are most comonly low-viscosity solutions of dyes (usually anionic) in water or water/alcohol mixtures with added glycols and wetting agents. Pigment-based inks are less-commonly used.
- laser printing, which is similar to xerography, but where the image is formed using a laser beam. The inks are also similar to xerographic inks, but also include styrene-butadiene and ethylene-vinyl acetate co-polymers.

Printing papers

This grade of paper products is sometimes referred to as graphical papers and usually includes those papers used for similar applications such as writing and copying. The term "printings/writings" is probably still the most common one for these grades, even though the writing application is probably much smaller today than the copying one. In total, this sector is the second largest after packaging papers/boards, accounting for about 40% of global paper production. These papers are normally classified into the two main grades:

- wood-containing papers, which are sub-divided into uncoated and coated grades
- wood-free papers, which are also sub-divided into uncoated and coated grades.

Problematic substances



Problematic substances are those that, either in their own right or through interactions within the process, cause various undesirable problems as summarised in the figure above. These problems are largely restricted to the wet end of the paper machine, but some of these issues are also relevant to the dry end, eg foam during coating. Corrosion is caused largely by dissolved substances, but can be accelerated by microbiological activity. Deposits occur in many forms and are caused either by the aggregation of substances already present in raw materials (stickies, pitch) or through the interaction between substances within the papermaking system (to form hydrolysates, slime, precipitates/scale). Foam is a different type of undesirable accumulation stemming from entrained gases that are stabilised by surface active substances. Insoluble complexes are formed through the specific interaction between anionic trash and cationic additives, but the most severe outcome of this interaction is the inactivation of the additive. As many of the problematic substances are water-soluble, these problems are usually worst on machines with closed water systems.

The impact of such problems will vary with the precise nature of each set of substances, but, unless controlled in some way, will ultimately lead to impaired machine runnability and impaired product quality, the latter leading to more broke (the re-use of which may further exacerbate problems and runnability) thus setting up a vicious spiral of ever-increasing difficulties. These sets of problems are best minimised by a common hierarchy of generic techniques (each being discussed further within each problem category):

- ❑ selecting raw materials with the lowest possible content of deposit-forming, interfering and surface active components

  This preventative approach should always be the preferred technique, but is often difficult to implement for 100% control, notably with problematic substances in recovered papers. An important element with such raw materials is the education of paper converters (and papermakers) of the need to consider the impact of all chemical additives on product recyclability.

- ❑ so far as it is practicable, optimising machine operation (without chemical addition) to minimise problematic interactions such as:
  - preventing dissolved solids reaching the paper machine by improved pulp washing or by simply thickening the thick stock and routing the filtrate away from the machine system
  - maximising the single pass retention of all problematic substances so that they do not build up
  - using and maintaining effective showering systems on machine fabrics
  - "good housekeeping" practises involving regular machine cleaning.

- ❑ dosing of specific control chemicals.

  Chemical dosing to cure what is largely a chemical problem in the first place has its dangers as, without close control, it may cure one problem and create another. Although chemical addition should only be used once the preceding preventative techniques have been fully explored, this technique is still very common, in some cases more as an insurance policy than an absolute necessity.

Propionic acid

This is one of a number of simple organic acids that can be generated within the papermaking system by certain types of acid-producing bacteria. It is a simple carboxylic acid with the formula CH_3CH_2COOH.

Proteins

Proteins are polymers of amino acids, which are connected by a peptide linkage (-CONH-). They are sometimes therefore referred to as peptides or polypeptides. The largest source of proteins in most papermaking systems is almost certainly within the bodies of micro-organisms, but protein-based or protein-derived products continue to be used and developed for papermaking as summarised below:

- ☐ gelatin, which was used extensively in papermaking going back some hundreds of years for sizing and strengthening the paper surface, but is little used today.
- ☐ casein, which is still used as a dispersant in rosin sizes and has also been used as a coating binder, but is now too expensive for the latter application.
- ☐ soy protein, which is used as a coating binder, mainly in North America. Soy protein contains a mixture of hydrophobic amino acids (eg aspartic and glutamic) and hydrophilic amino acids (eg leucine and alanine). Mild extraction from soybeans gives the largely intact protein, but this can be hydrolysed with alkali to improve its rheological properties or chemically modified to improve its binding power. The protein is supplied in powder form and has to be dissolved in hot water, usually with alkali in the form of sodium or ammonium hydroxide to give 10-25% solids content. Even though the alkaline pH means that the protein will be in an anionic form in the coating mix, the initial interaction between protein and pigment can cause some flocculation, but this is minimised by chemical modification. Addition rates are up to about 10% of the coating formulation. Protein-based coatings can be made water resistant by addition of insolubilisers such as glyoxal or formaldehyde.
- ☐ whey-derived proteins for detackifying pitch/stickies particles, which is a very recent development from one supplier. The amphoteric properties allow the protein to interact with other charged substances and thus the treated stickie particle can be retained in the paper using a suitable (normally cationic) polymer.
- ☐ enzymes, which have begun to be used for a few papermaking applications over the last 20 years. One part of the cellulase enzyme's structure is its cellulose-binding domain, which is responsible for keying into the cellulose substrate. These have begun to be explored over recent years as a means of introducing different functionalities into paper.

Proton

This is the positively-charged mass in the nucleus of the atom. Hydrogen contains just one proton in its nucleus and one electron, so the hydrogen ion, H^+, is in fact a proton. Strictly speaking, hydrogen ions do not exist as such in aqueous systems as they are always hydrated to give the hydroxonium ion, H_3O^+.

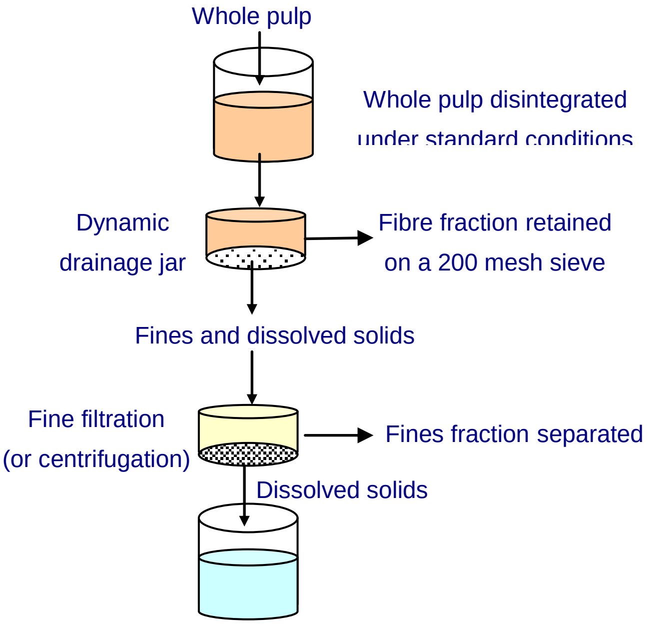
Pulps

This term is a very general one for the fibrous part of the papermaking furnish and is applied to both virgin and recycled materials. The fibrous pulp for making into paper may be prepared on the same site as the paper (integrated production) or on a separate site (non-integrated production), although this terminology is mainly used in the virgin pulp sector. Pulp characteristics are of obvious importance in relation to the quality of the final paper, but also in relation to the pulp's behaviour during the papermaking process. The strength characteristics of the pulp are its most important contribution to the properties of all paper grades and this is determined by the balance of genuine fibres and fines in the pulp and their physico-chemical characteristics.

For all types of pulp, their papermaking qualities can be considered under two quite different, but inter-related, headings:

- the functional qualities needed for that particular paper grade in terms of strength, brightness, light-scattering, etc
- the qualities that maximise the productivity of the paper machine in terms of ease of water removal and good runnability.

There is usually a strong focus on the end-use properties of pulps and this is reflected in the normal techniques of pulp evaluation, which concentrate on physical, rather than chemical, pulp properties. Pulps are normally evaluated by the pulp producer or the papermaker for their papermaking potential by preparing handsheets in the laboratory, usually covering a range of refining levels. Pulp chemistry features little, if at all, in most evaluations of this type, but there are a few exceptions, eg conductivity has to be evaluated in the case of electrical insulating papers and freedom from specific chemical contaminants in the case of photographic papers.



As shown in the diagram at right, pulps can be evaluated in terms of their wet end chemistry by disintegration under standard conditions appropriate to each paper machine and then separated into three fractions. The classification of the particulate fraction between genuine "fibres" and fines is normally carried out using the Dynamic Drainage Jar, but more sophisticated breakdowns of the particle size distribution of pulps can be conducted using the Bauer-McNett classifier or an automatic fibre length analyser.

The chemistry of the pulp's particulate fractions is important in relation to wet end chemistry and it should be useful to measure at least the following parameters:

- the zeta potential and the content of charged substances in relation to the aggregation of fines and adsorption of additives
- the ash content (mainly pertinent to recycled pulps) and its chemical nature
- pitch content of virgin pulps in relation to deposition problems on the paper machine
- stickies content of recycled pulps in relation to deposition problems on the paper machine
- microbial content of all pulps in relation to slime and related problems on the paper machine.

Being a relatively small, minor fraction, the content of soluble materials in pulps is often neglected, but can again be very important in relation to wet end chemistry. Whereas a very high proportion of the raw fibre's particulate materials end up in the papermaking pulp, the proportion of dissolved solids present in the pulping/bleaching circuits that are retained in the papermaking pulp depends critically on the pulp washing efficiency.

Economically, the pulp producer has a vested interest in routing as much as possible of the dissolved solids with the pulp as this maximises the apparent yield. However, most of these solids then dissolve on the paper machine and, unless the paper machine operates a very closed water system, they will be poorly retained in the paper. Moreover, the dissolved solids (depending on their nature) will probably also contribute to various problems as they circulate around the papermaking circuits before leaving, perhaps in a different chemical form, mainly in the machine wastewater. It is thus desirable that all pulps (including perhaps some grades of machine broke) are washed as well as they can be before passing to the paper machine directly (at integrated mills) or being dried for transport to another mill. This important topic is discussed further under washing.

Unlike the particulate fraction, where there is a standard procedure for determination of fibre/fines, there is no standard technique for dissolved solids, for which their extent of dissolution depends on several parameters such as temperature and the electrolyte content of the dilution water. It would useful for every mill to develop a standard dissolution procedure, which reflects the conditions on its own paper machines. In most situations, it would be valuable to measure at least the following on the resultant dissolved solids (separated by standard filtration or centrifugation):

- pH and acidity or alkalinity
- conductivity and the concentration of selected ions such as calcium
- total concentration of organics as COD or DOC
- individual organic compounds such as carbohydrate, starch or organic acids
- charge demand (usually cationic) by titration with oppositely-charge polymers.

When doing this work in the laboratory using a dry pulp or one of known moisture content, it is best to normalise the measured concentrations to kg substance/tonne pulp dry solids.

PVA

This is one abbreviation for polyvinyl alcohol, but as it is also sometimes used for polyvinyl acetate, it is best avoided in order to avoid confusion.

PVAc

This abbreviation is sometimes used for polyvinyl acetate.

PVOH

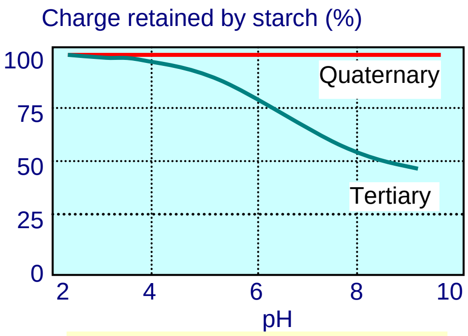
This is the preferred abbreviation for polyvinyl alcohol.

Quaternary ammonium compounds

These are quaternary nitrogen compounds in which there is just one nitrogen atom and have the general formula $R_4N^+ Cl^-$. They are used in papermaking as biocides and as softeners.

Quaternary nitrogen compounds

These are a type of organo-nitrogen compound in which the nitrogen is attached to four carbon atoms and thus always has a positive charge. This is in contrast to primary, secondary and tertiary nitrogens (as in polyethyleneimine and polyvinylamines) where the charge on the nitrogen is pH dependent (see example at right for cationic starch). Quaternary nitrogens are found in many polymers used in papermaking as they confer a stable cationic charge on the polymer chain, eg cationic polyacrylamides, polydadmacs, polyamines, cationic starch and polyamideamino-epichlorhydrin resins. Quaternary nitrogen compounds in which there is just one nitrogen atom are called quaternary ammonium compounds.

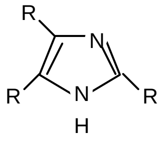


Source: Harvey in 1987 Tappi
Wet End Chemistry Seminar Notes.

Quenching

This is a term for the interaction between an fluorescent brightener and a substance that neutralises its functionality. As brighteners are anionic, the most common types of quenching agent are cationic materials, which are often present in the form of other chemical additives (retention aids, dry or wet strength agents, etc). When brighteners are being added at the wet end, this quenching interaction is obviously undesirable and should be minimised by, for example, keeping addition points as far apart as possible.

In other cases, it may be desirable deliberately to neutralise the fluorescent material (eg from returned broke) and this can be done effectively with chemicals such as the substituted imidazolines (shown at right in non-protonated, neutral form). The fluorescence of brighteners can also be destroyed by treatment with chemicals that are used for bleaching deinked pulps and coloured broke. Oxidising bleaches such as chlorine/hypochlorite, chlorine dioxide and ozone are very effective at this, but other bleaching agents such as hydrogen peroxide or the reducing bleaches sodium hydrosulphite and FAS are not effective.



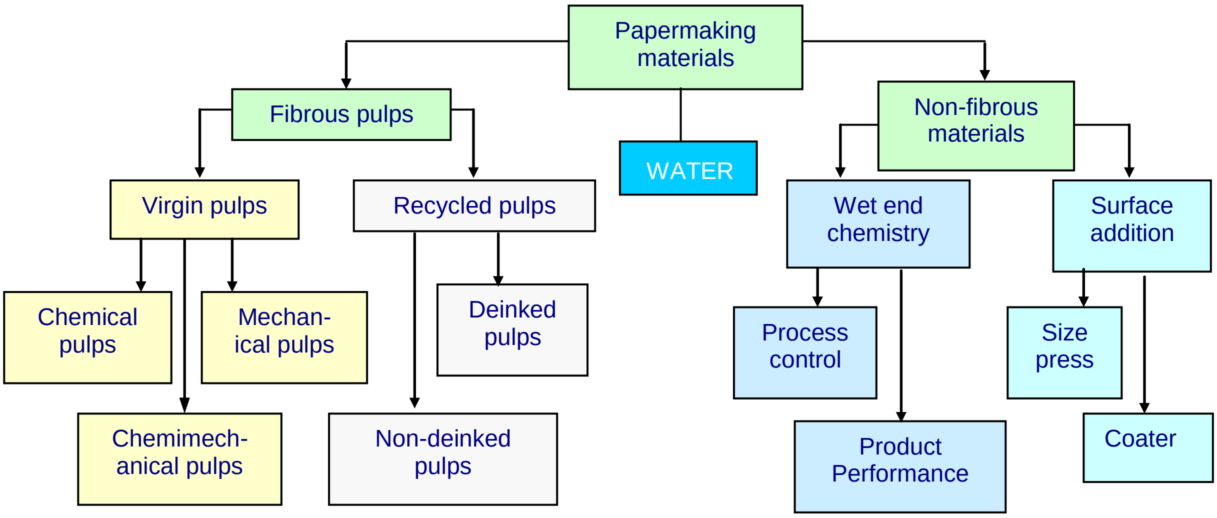
Radius of gyration

This term is used to describe the size of polymer molecules in solution. The radius of gyration (R_g) is the root mean square distance of all the polymer segments from its centre of gravity:

$R_g = (1/n_i \Sigma r_i^2)^{0.5}$ where n_i = number of units in chain and r_l = distance from the centre of mass

Depending on the conformation of the molecule, the radius of gyration can be estimated from the length of each unit. For a IM Dalton polysaccharide, it is about 900 nm for an extended rod (ie a highly-charged polymer) and about 20 nm for a randomly-coiled (ie nonionic) polymer.

Raw materials



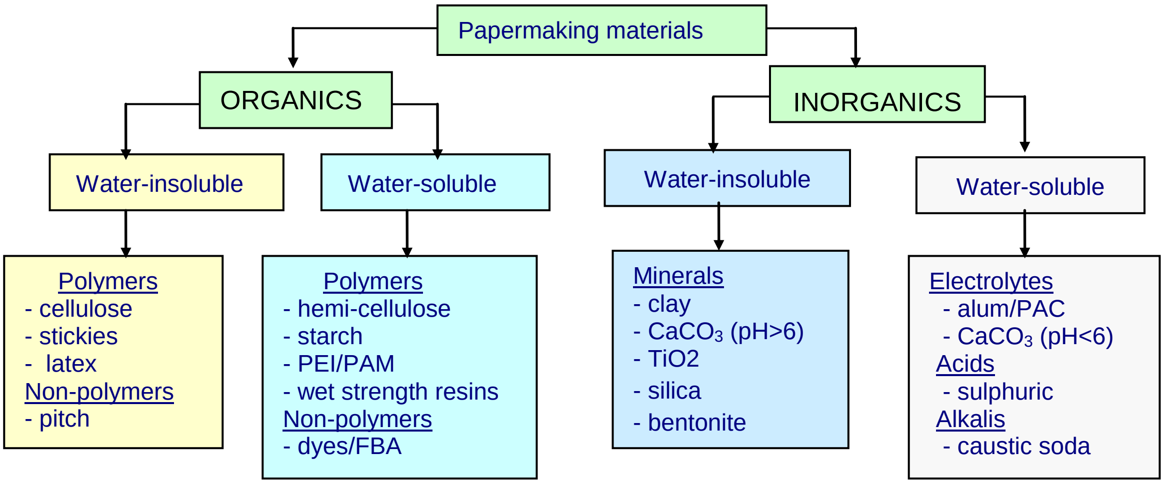
As shown above, the materials present in the papermaking system can conveniently be divided into two main groups plus one unique material:

- fibrous components, usually referred to as pulp, which may be either virgin or recycled
- non-fibrous components, which includes every raw material other than pulps except
- water, the unique raw material that is universally present throughout the papermaking system and whose influence is often under-estimated, particularly within wet end chemistry.

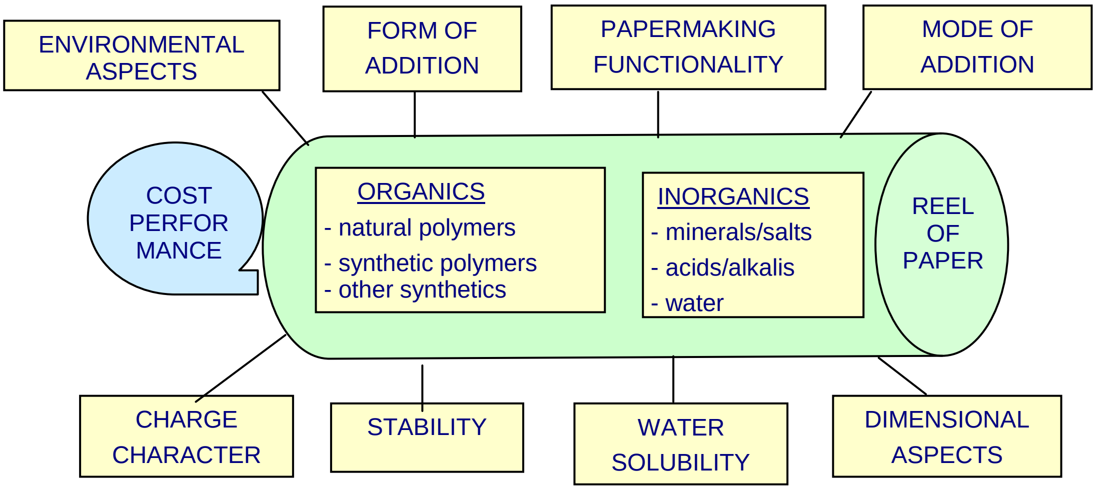
Pulps are always added at the wet end as they form the backbone of all paper products, but non-fibrous materials can be added either at the wet end or to the paper surface. This distinction is very important not only in terms of the functionality of the additive in the product, but also in terms of the additive's retention. The overall retention of wet end additives is complex, whereas the retention of surface-applied chemicals is essentially 100% at the point of application. Most raw materials are added at the wet end, but when pulps are excluded, the balance between wet end and surface addition is much more balanced.

Papermaking raw materials can also be classified in terms of their broad chemical character between organic and inorganic materials. The breakdown shown below uses a further sub-division in terms of the material's water solubility, which is very important for wet end additives as it determines their retention mechanism and pattern of build-up when the water system is closed up. A unique characteristic of particulate raw materials is that they have a surface which can interact with other particulates or with dissolved substances. These interactions depend on the available surface area and chemistry of the surface and this important area is discussed further here.

Raw materials could be classified in many other ways in terms of key attributes, some of which are shown in the more general scheme below. Many of these attributes will be at the centre of why raw materials are selected to do a particular job in the first place:



- cost-performance to deliver that functionality either within the process or in the product is always likely to head the list, where cost should include the desired level of service required from the chosen supplier. A key aspect within this area is information about the nature of the raw material's dose - response relationship, where dose should be understood in both mass and cost terms. The functionality of the raw material will also bring in issues to do with its charge character, water solubility and dimensional aspects. The mode of addition (wet end or surface application) will be dictated by the particular functional effect allied to what is possible on a particular paper machine.
- material form, which usually means either a dry or liquid product, the distinguishing practical factor being whether the product is pumpable or not. In papermaking, there is an ongoing trend towards liquid products, even for products that are obviously solids (eg fillers), due to the ease of handling and dosing. Selection between these two extremes should always include an assessment of wider issues such as environmental effects (eg transportation of water) and process implications of any auxiliaries (eg dispersants in filler slurries).
- the environmental aspects of raw materials is an area of steadily-increasing importance with broader forms of legislation and voluntary adoption of environmental management systems.



Reaction chemistry

This involves the formation of new chemical bonds between reactants. However, there is little deliberate use of reaction chemistry in papermaking chemistry as most chemical additives are manufactured in a ready-to-use state and all the papermaker has to do is to retain them in the sheet. However, chemical reactions (albeit rather simple ones) do take place at the wet end, but these are generally undesirable ones leading to various problems such as:

- ❑ hydrolysis of additives such as AKD and ASA sizes to less- or non-functional form
- ❑ dissolution of calcium carbonate.

Chemical reactions are much more important in a positive sense in the drying section and are essential for some additives (eg sizes and wet strength resins) to cure and thereby express their desired functionality.

Recovered paper

This is the source of one of the two broad categories of papermaking pulp, in this case of recycled pulp. Globally, about 150M tonne of used paper was recovered for re-use in 2001, the vast of majority of which was used for material recycling back to paper mills. Not all of this material actually reaches the forming part of the paper machine due to the substantial losses in preliminary cleaning processes. Paper recovered for recycling can be classified into two broad classes:

- ❑ pre-consumer material that never reached the final user, eg converting off-cuts, printers waste, machine broke, etc.
- ❑ post-consumer material that has actually been used for its intended purpose with various further sub-divisions such as white wood-free printed or unprinted, container waste, mixed papers, etc.

Pre-consumer recovered paper is inherently cleaner than post-consumer recovered paper as it should contain only what has been added during papermaking, whereas the latter can contain virtually anything. There are three different routing possibilities for different grades of recovered paper:

- ❑ genuine **re**cycling into the same grade, eg old corrugated containers into more liner or fluting
- ❑ **down**cycling into a product with a less demanding specification, eg printings into towels
- ❑ **up**cycling into a product with a more demanding specification, eg brown packaging papers can be upgraded for use in white papers (albeit by the use of a process which is not that different from bleaching unbleached virgin fibres).

Depending on the grade of paper being made, recovered papers can be re-used on the paper machine in two different ways:

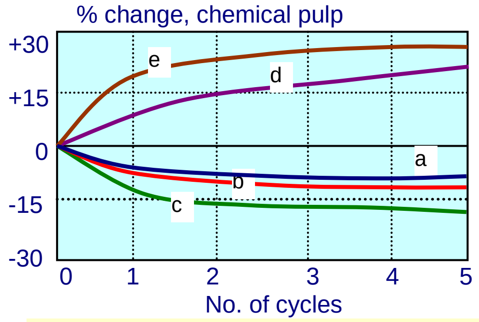
- ❑ after mechanical cleaning as part of the normal stock preparation system. This mainly applies to recovered paper being recycled into packaging grades, but this would also be the normal route for pre-consumer recovered papers. Such recycled pulps will be referred to as non-deinked pulps in this document, although they are also sometimes referred to as "direct entry" pulps.
- ❑ after deinking in an off-machine process to produce a deinked pulp. Like virgin pulp mills, deinking plants can be fully or partly integrated with paper production on the same site or be completely separate for the production of market deinked pulp. Deinking is applied principally to recovered paper being recycled into wood-containing printing/writing papers (eg newsprint), tissue and towel grades, wood-free fine papers and certain packaging products (eg the liner in white-top grades).

The generic chemical characteristics of the pulps produced from recovered paper are described under recycled pulps and the more specific attributes of the two main types are then described further under non-deinked pulps and deinked pulps.

Recyclability

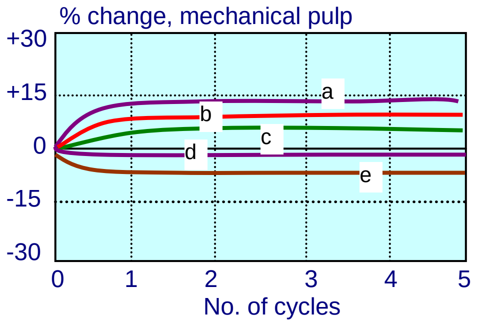
This term has no standard definition, but can be taken to refer to the value of recovered paper when it is recycled to make more paper. As recycling of recovered paper is largely concerned with recycling of the fibrous component, recyclability mainly refers to the papermaking value of this component in the recovered paper. Much research has been carried out on the effects of recycling on fibre characteristics (notably strength) and it is now well-established that there are substantial differences between mechanical and chemical pulps, which are due to the difference in their lignin content.

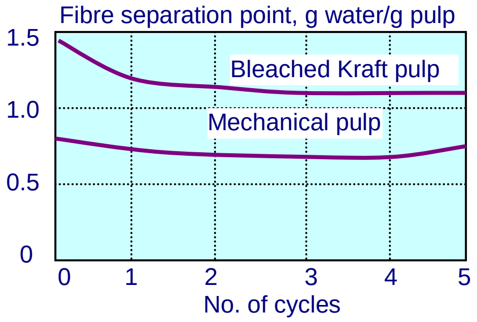
When a paper comprising chemical pulp is dried, the fibre collapses and the hydrogen bonds that are formed between cellulose hydroxyls are not accessible to water when the paper is re-slushed. This occurs to some degree if virgin pulp is first dried, as shown in this example of the difference in the adsorption of cationic starch between a dried and never-dried pulp. However, the effect is greater after the pulp has been refined. This stiffening of chemical pulp fibres is called “irreversible hornification” and results in a loss of swelling ability and strength when such fibres are recycled, as shown in the figure at right. Although the elevated drying temperature has an adverse effect on swelling, it is the loss of water beyond the fibre saturation point that causes the collapse of the lumen and loss of swelling ability.



Reference: Howard and Bichard, J.Pulp Paper Science, 1992, 18, 4, 151-159.

a - sheet density b - tensile strength
c - burst strength d - tear strength
e - scattering coefficient



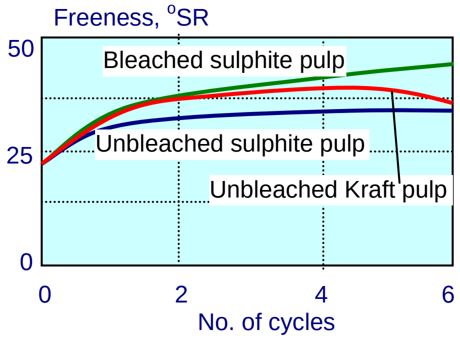


By contrast, mechanical pulp fibres appear to flatten during recycling, but with no formation of irreversible hydrogen bonds across the lumen. This flattening increases the bonded area and accounts for the oft-observed increased strength of mechanical pulp fibres on recycling (as shown in figure at left, where the parameters are are the same as in the first figure). This strength loss occurs without any loss of swelling ability, unlike the case of chemical pulps (see figure at left below).

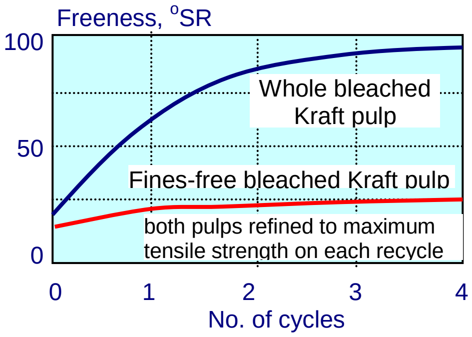
Chemi-mechanical pulps exhibit similar trends on recycling to full mechanical pulps, but, as for full chemical pulps, the change on the first recycle is more significant. The changes in strength properties do not result from changes in the inherent strength of the fibres for either mechanical or chemical pulps. The changes in light scattering follow from the changes in strength, reflecting the changes in inter-fibre bonding and hence in the number of air-fibre interfaces. Whereas the improvement in strength for mechanical pulps is accompanied by an increase in sheet density (less bulk), the loss of strength for chemical pulps occurs at the same time as a reduction in sheet density (higher bulk).

One of the important variables in recycling is the degree of mechanical treatment given to the recycled pulp. The data in the above figure showing the effect of recycling on swelling (fibre saturation point) is for a disintegrated, but unrefined, mechanical pulp, but the chemical pulp was refined. All papers were made without the use of retention aids, but whitewaters were recycled to build up the fines to equilibrium levels before producing sheets for testing. However, this procedure was shown not to affect the trends on recycling, but it did affect the level of strength achieved (this being greater in the fines-retained sheets). The unrefined chemical pulp showed an actual increase in tensile and burst strengths on recycling, which was attributed to decurling of the fibres, a characteristic of some dry lap bleached chemical pulps. In the absence of this effect, refining tends to exacerbate strength loss on recycling due to the greater internal fibrillation creating internal hydrogen bonds that are not broken down on subsequent re-slushing.

Generally, it is found that, when fibres are simply disintegrated during recycling, the freeness of the resultant stock is similar to, or perhaps slightly higher than, the original pulp. However, when the fibres are refined, usually in order to improve the strength of the recycled paper, the freeness gets worse (as shown in the figure at right) and the fines content increases. When the fines are removed from the pulp before refining (as occurs to some degree in deinking), the freeness of the fines-free fraction is little changed by recycling, as shown in the figure below at left. Limited data on the effects of other papermaking operations such as pressing and calendering indicate that these operations reinforce the effect of refining through compressing the fibres and introducing further hornification.



Reference: Howard, Paper Technology, 1991, 32, 4, 20-25.



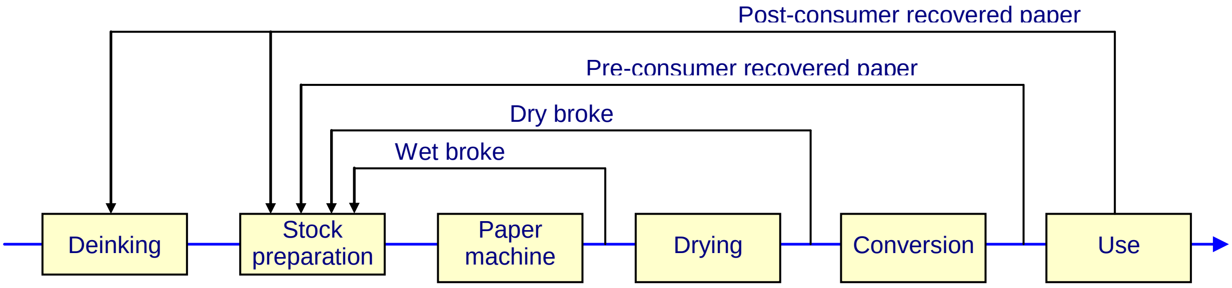
The chemistry at the wet end during the first making of a pulp into paper affects the characteristics of the fibre when it is recycled. In line with the explanation about the effect of pH on fibre swelling, the wet end pH during the first making affects the subsequent swelling of papers made from recycled unbleached chemical pulps, but not of bleached chemical pulps, although this will depend on the content of anionic groups and their dissolution during recycling. Alkaline treatment is a technique used to upgrade recycled fibres in non-deinking systems because of its beneficial effect on swelling, notably for pulps with a higher content of charged organics (eg the unbleached NSSC flutings and Kraft linerboards that are recycled in old corrugated containers).

The recyclability of non-fibrous components in recovered papers is rarely discussed or valorised, but they will contribute a substance-specific background effect although their efficacy is not easily predictable and cannot be relied on. Any filler or pigment present in a recycled pulp will be able to express its functionality, the only constraint being the loss of any calcium carbonate filler through its dissolution under acid conditions. However, as for added virgin filler, the efficacy of the recycled filler will be affected by its state of aggregation. The limited data on recycling of sized papers indicate adverse effects due to the slowing down of the rate of water penetration during pulp slushing/disintegration, unless they are hydrolysed by chemical pre-treatment (eg high or low pH depending on size chemistry). Even if size residues are retained in the paper made from recycled pulp, they are not likely to be optimally oriented for sizing and they may also interfere with inter-fibre bonding. For rosin-sized recovered papers, the presence of dissolved aluminium species would have some adverse effect on fibre swelling.

Most other non-fibrous additives are added as water-soluble chemicals and will only be classifiable as recyclable if they remain attached to the particulate matrix and are thereby retained in the new product. The most common type of strength agent in recovered paper is various forms of starch, which are mainly in-mill converted starches added at the size press. Such starches are poorly adsorbed by the particulate matrix and cannot thus be considered recyclable. The only starches that are recyclable are cationic starches, but even these may be desorbed during any bleaching stages in deinking or broke decolorisation and through microbial action at the wet end. If they are cationic, polyacrylamide-based strength agents are more likely (than cationic starches) to be retained in view of their non-biodegradability.

The recyclability of wet strength agents is rather an academic point as most wet strengthened papers are not recovered for recycling, but, even for those that are, they cannot be classified as recyclable as the wet strength agent has to be broken down chemically in order to disperse the fibres. Dyes in recovered papers may contribute to the colour of new products, but this is often undesirable and colour-stripping of recovered papers, usually as part of deinking systems, is common. Dyes in machine broke are more recyclable as the papermaker can segregate this material and re-use it on grades where the dye contributes to the colour of a like-coloured or colour-compatible grade. Being anionic chemicals, fluorescent brighteners are not recyclable due to their ease of water solubility, particularly so for the grades used in greatest quantity at the size press. Variable fluorescence in products may demand deliberate quenching of residual brightener.

Recycled pulps



All recycled pulps are derived from paper that has at least reached the reel-up stage of the paper machine. Materials that are re-used from earlier stages in the form of wet trim and sheet breaks are not classed as recycled pulp as they have not been through the dryer section and are always re-used immediately within the same making. All paper machines have to contend with recycled pulps in the form of their own dry broke, which can be a major source of variability, particularly when it contains surface-applied chemicals. The chemistry of some papers changes after reel-up due to the continuation of curing reactions in some sized papers and in all wet strengthened papers. Apart from this and of possible microbiological changes if the paper is stored in wet or moist conditions, the chemistry of the paper is fairly stable throughout any converting stage(s) and during storage and use.

Recovered pre-consumer paper has similarities to machine broke in that it should be reasonably clean and only contain papermaking materials. By contrast, recovered post-consumer used papers are much more heterogeneous through mixing together sometimes very different grades from many manufacturers and through the presence of non-papermaking materials (eg inks, converting adhesives, etc). Recycled pulps are thus very different from virgin pulps on several counts:

- the pulp fibres will have been through the papermaking process at least once before and this will have changed some of their key physical properties such as strength
- the soluble materials from the original wood pulp will be largely absent, as they will probably have been poorly retained in the previous making(s) (but this depends critically on the degree of water closure of those machines)
- non-fibrous raw materials will be present from the previous making, although this fraction is completely or partially removed prior to papermaking if the pulp is deinked prior to use
- residues of materials added during any pre-treatment of the pulp (eg deinking) may be present.

Much research has been carried out on the effects of recycling on fibre characteristics (notably strength) and it is now well-established that there are substantial differences between mechanical and chemical pulps due to their different in their lignin contents. This is discussed further under recyclability.

There are two very important practical issues regarding the use of all recycled pulps:

- the lower inherent strength potential of recycled compared to virgin fibres

  This means that papers made with recycled pulp will probably need greater use of strength additives such as starch. The strength of the recycled pulp can partially be recovered by refining, but there is usually some reluctance to refine recycled pulps as much as virgin pulps because the unrefined pulp already has a relatively high fines content.

- the presence of problematic substances in the recovered paper.

  This is more of a problem for non-deinked pulps as the process of deinking has the potential to remove most of these substances prior to the pulp reaching the paper machine. The most significant problematic substances in recycled pulps are chemicals applied in previous makings to the paper surface at the size press, in coating and in converting operations.

The most significant problematic materials in bought-in recovered paper and machine broke are:

- size press starches

  These range from in-mill converted native starches to supplier-modified starches with varying chemical functionalities. These starches are likely to be the most significant source of dissolved organics at the wet end on many paper machines. The size press starch content of broke and recovered papers varies from zero for grades such as newsprint up to 4-6% for wood-free printing/writing grades and corrugated case materials.

- dispersants in slurry-supplied fillers and coating pigments.

  These dispersants are normally anionic polymers such as polyacrylates, which have a very high cationic demand. Dissolution of such substances represents a major disturbance to the wet end chemistry on machines making coating base papers and thus receiving coated broke, but less so on machines using recovered paper as the content of coated papers is less significant.

- adhesives used in the conversion of mainly packaging grades

  These give rise to deposition of stickies if allowed to penetrate into the papermaking system. Apart from the starch-based adhesives used to glue the liner and fluting in corrugated cases, other converting adhesives bear some similarity to some of the binding chemicals used in printing inks, there being two main types:
  - hot melt adhesives which bond at elevated temperatures.
  - contact adhesives which bond at ambient temperature with applied pressure.

- coating binders.

  These are based on synthetic latices such as those based on styrene-butadiene, acrylates and polyvinyl acetate. When recycled as coated broke, these latices are present at high enough levels to give rise to a specific type of deposition problem known as white pitch. All coating materials with some hydrophobic character (eg silicones, waxes, etc) can give rise to wet end contamination problems not dissimilar to ordinary pitch and white pitch. On recycled machines, the proportion of coated paper is usually insufficient to distinguish any deposition due to white pitch from deposition due to stickies.

- microbial content

  This varies widely (10^5 to 10^{10} CFU/g) depending on source with mixed grades of recovered paper being the most contaminated.

The main practical distinction within recycled pulps is whether deinking is necessary and this depends largely on the grade of paper being made judged against the quality of the appropriate grades of recovered paper. The papermaking quality of non-deinked pulps should not be considered inherently inferior to that of deinked pulps although some of the chemical conditions commonly present in deinking (eg alkaline pH) can improve certain fibre qualities (eg strength) and some of the unit processes (eg flotation) can enhance the removal of some problematic substances (eg stickies). Those paper grades made from non-deinked pulp would not have a significantly superior quality if they were made from deinked pulp (using the same grades of recovered paper), although the papermaking process may have better runnability due to the higher removal of some problematic substances, particularly those that are dissolved. Deinking is thus used only where it is necessary, not least because of the extra complexity and costs involved. The chemical attributes of deinked and non-deinked pulps are discussed further under their respective headings.

Recycled water

The water used on the paper machine is a mixture of fresh water and water recycled after some previous use. Water recycling is an inherent part of papermaking on virtually all machines and is the main way to lower fresh water use and maximise the degree of water closure with its attendant benefits and difficulties (see this summary). The most important water recycling loop is the primary loop (see this diagram) as this contains most of the substances not retained in a single pass through the formation wire. Chemical additions might be made to the water recycled in the primary loop for control of foam and microbial problems. Similar additions might also be made to the much smaller flow in the secondary loop, which, if it incorporates a flotation saveall, would involve addition of flocculants with a similar chemistry to the range of polymers used as retention aids.

Water may also be recycled after external wastewater treatment in a tertiary loop. Whereas the chemistry of the liquid phase in the water recycled in the primary and secondary loops is similar to that in the thick and thin stocks, the chemistry of the treated wastewater will be different depending on the extent of treatment provided. It is outside the scope of this document to elaborate details of the many different wastewater treatment processes, but this can be summarised briefly as follows and pictured in the diagram below:

- primary treatment processes

  This first stage of treatment is directed at removal of suspended particulate solids using either sedimentation, flotation and filtration sometimes with assistance from chemical pre-treatment for aggregation of fines.

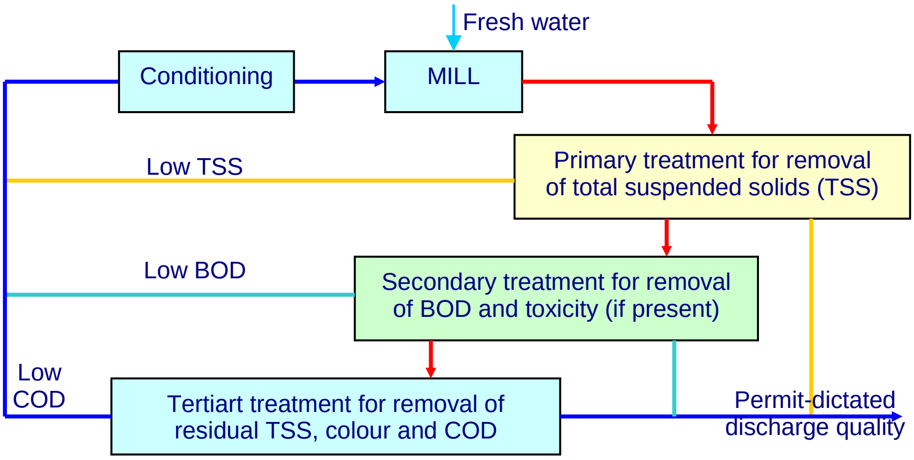
- secondary treatment processes

  Having lowered the suspended solids to reasonably low levels (<100 mg/l), the second stage of treatment is aimed at removing that fraction of the dissolved organics which is biodegradable (the BOD - biochemical oxygen demand). This is achieved using biological treatment in different types of reactor, there being two main types operating either aerobically or anaerobically. The main chemical addition to this stage is phosphorous (in the form of phosphate) and nitrogen (in the form of urea) nutrients for the biomass.

- tertiary treatment processes

  This stage can take on a variety of forms depending on local issues, which may be related to factors related to external discharge or internal recycling. The most common treatments are:
  - removal of residual suspended solids (using similar processes to the primary stage)
  - removal of lignin-related colour (using chemical precipitation/adsorption techniques)
  - removal of residual nutrients, notably phosphate, again using chemical precipitation
  - removal of non-biodegradable organics (as COD).

The most common type of wastewater for recycling to the paper machine is the secondary-treated wastewater, which has quite low levels of dissolved organics, but where the inorganic electrolytes are often relatively unchanged from the raw wastewater. One of the more significant electrolyte components is dissolved calcium, but this is also one ion that can be removed during the biological stage of wastewater treatment. This occurs primarily as a result of pH shifts and release of carbon dioxide, but the wastewater is often still unstable in terms of further calcium carbonate precipitation. Because of these factors, wastewaters may be treated further than is necessary (conditioned) to meet discharge requirements in order to lower electrolytes (notably calcium), colour and also to eliminate microbial content by disinfection.



Internally and externally-recycled waters are re-used for various applications:

- ❑ simple stock dilution, but most of this requirement is met by the waters recycled within the normal primary and secondary loops (see this diagram).
- ❑ wire and press section showers, which require water of varying qualities (depending on pressure), mainly in terms of particulate solids, but some dissolved solids such as temporary hardness may also be important.
- ❑ sealing of vacuum pumps and gland sealing of rotating elements, which requires water of comparable quality to that for showers.
- ❑ general-purpose cleaning such as hose water, which does not require very high quality water
- ❑ chemical make-up or dilution, which requires water of good quality and is normally fresh water. However, recycled waters are beginning to be used for this purpose (see dosing).

Redox potential

This is an important concept within electrochemistry and may be useful to measure in some papermaking systems as it provides information about the degree of oxygenation, which is relevant to microbiological activity. Each reduction-oxidation (redox) couple is characterised by a redox potential (E_H), which can be calculated using the Nernst equation:

For the couple: $A + ne^- \rightarrow A^{n-}$

$$E_H = E_H^o + 2.3RT/nF.\log [A]/[A^{n-}]$$

where R = gas constant = 8.314 Joule/mole.°K, T = absolute temperature (°K)

and F = Faradays constant = 96,490 Coulombs so that 2.3RT/F = 0.059 volt/mole at 25°C.

By convention, redox couples are always written as a reduction with the electrons on the left-hand side. The standard electrode potential (E_H^o) is the potential when the oxidised and reduced forms are at unit concentration (activity). Individual couples cannot exist in isolation and are always measured relative to the standard reference couple which is the hydrogen electrode:

$$2H^+ + 2e^- \rightarrow H_2\text{, where } E_H^o = 0 \text{ volts at } 25^oC$$

This electrode comprises a platinum electrode immersed in an aqueous solution of hydrogen ions in contact with hydrogen gas. As this set-up is not the simplest to arrange practically, other electrodes tend to be used for reference purposes in the laboratory, notably the silver-silver chloride electrode or the calomel electrode.

Couples with positive standard potentials are oxidising systems:

$$\text{eg } Cl_2 + 2e^- \rightarrow 2Cl^- \text{ where } E_H^o = +1.4 \text{ volts at } 25^oC$$

Couples with negative standard potentials are reducing systems:

$$\text{eg } Na^+ + e^- \rightarrow Na \text{ where } E_H^o = -2.7 \text{ volts at } 25^oC$$

The thermodynamic condition for the complete oxidation-reduction reaction to take place is:

$$\Delta G = -nFE > 0\text{, which occurs when } E > 0\text{, where E is the potential of the complete reaction}$$

The standard electrode potentials for the various redox couples (sometimes referred to as the electrochemical or galvanic series) are useful to judge the ability for such reactions to be thermodynamically possible, but this does not mean that the reaction will take place due to the actual reaction conditions (concentrations, temperature) being different from the standard conditions, due to kinetic limitations and due to polarisation effects.

Reduction

In chemistry, this is part of an overall process of transferring electrons between substances and reduction of one substance is always accompanied by oxidation of another substance. A reducing agent like hydrogen has the ability to donate electrons as follows:

$$H_2 \rightarrow 2H^+ + 2e^-$$

These electrons can then be accepted by an oxidising agent like oxygen:

$$½O_2 + 2H^+ + 2e^- \rightarrow H_2O$$

and the overall reaction can be written as $H_2 + ½O_2 \rightarrow H_2O$ in which the hydrogen is oxidised and the oxygen is reduced to water. The ability of the reaction to proceed is determined by its redox potential. Reducing chemicals in papermaking include the bleaches sodium hydrosulphite and formadine-sulphinic acid (FAS).

Refiner mechanical pulp (RMP)

This type of mechanical pulp is produced by a process that developed from the use of refiners for mechanical treatment of the rejects from groundwood processes. The first plant was installed in about 1960, initially operating at low consistency, but most processes now operate at high consistency (40-50%) due to the higher pulp strength achievable. In the RMP process, the wood chips pass between two grooved plates, one of which is rotating at about 1500 rpm and the other static in single disc refiners and both of which are rotating in double disc refiners. This process has largely been overtaken by the thermo-mechanical pulping process, which uses similar equipment, but achieves higher pulp strength and a lower shives content.

Refining

This is the term for the mechanical treatment of the pulp, which is primarily carried out to develop its strength and normally takes place soon after initial pulp slushing. The older terminology for this process is beating, which reflects the use of a different type of equipment. Refining is mainly carried out on bleached chemical virgin pulps and recycled pulps. Mechanical pulps are usually not refined as this would cause excessive fibre shortening rather than strength development due to their high lignin content and resultant stiffness. The refining process is usually controlled by observing the change (decline) in the freeness properties of the stock using the well-known Schopper-Riegler (SR) or Canadian Standard Freeness (CSF) tests.

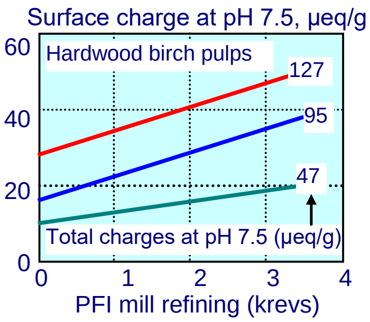
In refining, the pulp suspension is passed through the small gap between a rotating set of bars (the rotor) and a stationary bedplate (the stator). The effect of the refining action on fibres is complex, but involves the following changes to the particulate pulp structure:

- ❑ removal of the less easily-swellable outer (primary and S1) layers of the fibre wall, thus facilitating access of water to the more easily-swellable parts of the fibre wall. However, this process contributes to the generation of secondary fines.
- ❑ fibrillation of the newly-exposed fibre surface (the thick S2 layer) with a large increase in external surface area plus internal fibrillation or delamination caused by the intake of water into the non-crystalline cellulosic regions. The fibres become more flexible so that they can conform to one another more easily during the later stages of water removal.
- ❑ shortening of fibres by cutting and tensile forces plus other changes in fibre shape such as straightening (of bent fibres), curling (of straight fibres), fibre stretching and the introduction of dislocations and micro-compressions.

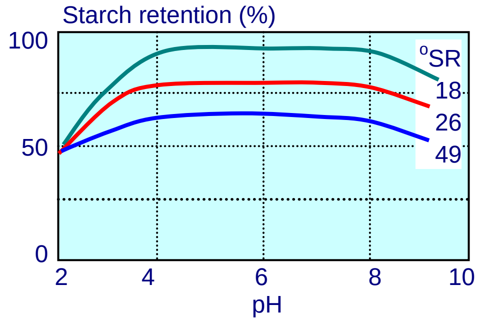
Overall, refining leads to increased fibre flexibility and fibre surface area available for bonding. Whilst the main strength properties such as tensile and burst strength are improved by refining, tear strength generally decreases due to fibre shortening. The closer, more uniform fibrous structure also leads to better formation, which further improves paper strength and to increased sheet density, which gives lower bulk, porosity and opacity.

During paper formation, however, the fine particles generated in refining have two major adverse effects – the impairment of single pass retentions and of water removal. However, the fines also introduce a potential benefit in providing an increased surface area for interaction with fillers and chemical additives. Examples of the effect of refining on sizing of bleached Kraft pulps is shown here in terms of reduced sizing at constant rosin dose and here in terms of the differences between fines from refined bleached hardwood and softwood Kraft pulps on AKD sizing. An example of the adverse effect of refining on water removal is shown here for an unbleached Kraft pulp.

In terms of wet end chemistry, one of the benefits of refining is that, by allowing the fibres to swell, it increases the accessibility to charged surfaces in the pulp. This is shown at right for three hardwood Kraft pulps with varying levels of total anionic substances. Over the range of refining levels, the fines content doubled from about 7% to 14% and the charges titratable by a polydadmac polymer (300k Daltons molecular mass) increased as shown, whilst the total charges remained reasonably constant. The results were similar with the fines removed prior to refining and indicate that previously inaccessible charged points within the fibre matrix become available for adsorption as refining proceeds. This should be beneficial to the adsorption of wet end cationic additives.



Source: Laine, J in Paperi ja Puu, 1997, 79, 4, 257-266..

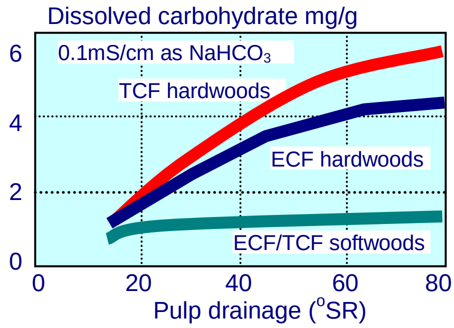


Source: Roberts J.Pulp Paper Science, 1987. 13. 1. 1-4.

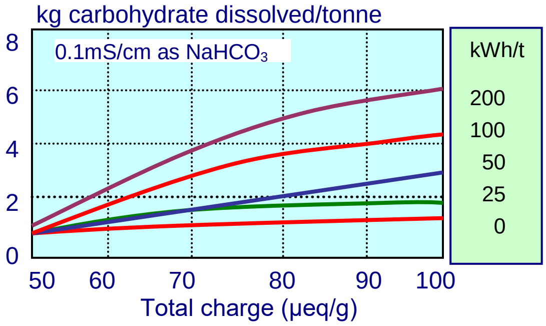
As a result of the generation of fines, the single pass retention of the refined pulp is always lower than that of the unrefined pulp, as shown by the increased flowbox concentration and declining total SPR in this example here. The diagram at left shows the effect of stock pH and refining level on the retention of a cationic starch (DS = 0.023). At any pH, increased refining lowers the starch retention because of the higher fines level and not because of any loss of starch adsorption. A high starch retention could have been maintained by the use of an effective retention aid with the dose increasing in line with the increased fines level.

In addition to the changes in the pulp's particle size distribution on refining, the other important impact is on the dissolution of water-soluble substances. Dissolution obviously depends in the first place on the pulp's content of potentially water-soluble materials, which varies with pulp type and previous history and, in the second place, on processing conditions such as pH, temperature and electrolyte concentration. As the pulp quality will itself affect some of these variables (eg pH) and the degree of water closure will also affect others (eg electrolyte concentration), it is difficult to predict the overall extent of dissolution of the different water-soluble materials on an actual paper machine. It seems likely that readily-soluble electrolytes in the pulp (eg chlorides from pulp beaching and the major pH determining ions) will dissolve under most conditions and that these concentrations will then determine the extent of dissolution of the more slowly dissolving organic fraction. An example is given here for dissolution from several recycled pulps on refining after simple slushing.

An example of some dissolution effects on refining is given in the figures below for a mixture of ECF and TCF bleached Kraft pulps. The dominant organic material with a potential for dissolution in all bleached Kraft pulps is the hemi-cellulose carbohydrate and the first figure at right shows the course of carbohydrate dissolution in terms of the normal index of refining, the pulp freeness. Dissolution is clearly greatest for hardwoods (particularly the TCF eucalypts although this is not shown), where over 0.5% of the pulp dissolves at high refining levels (but low electrolyte levels). Increased electrolyte levels decrease dissolution as they suppress the swelling of fibres (see examples here for ECF pulps and here for TCF pulps from the same study).



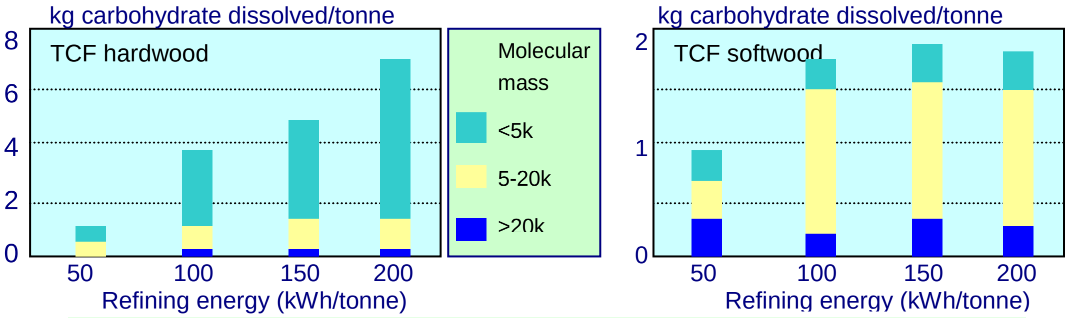
Source: Sjostrom in Nordic Pulp Paper Research J, 2000, 15, 5, 469-475.



Reference: Sjostrom et al Nordic Pulp Paper Research J, 2000, 15, 5, 469-475.

At a fixed electrolyte level, dissolution of organics depends on the refining level and the charge content of the pulp. Again, this is due to the positive effect of pulp charges on the pulp's swelling behaviour. This is illustrated in the figure at left for a range of ECF and TCF pulps with different contents of anionic substances. It is evident that anionic substances in the pulp increase the overall dissolution at any refining level, but this is greatest at the highest level of refining.

There are differences in the molecular size of the dissolved substances between different wood types and different refining levels (see figure below). The dissolved organics from softwoods (ECF or TCF) are predominantly "medium" molecular mass polymers (5-20k Daltons), whilst that from hardwoods is predominantly "high" molecular mass polymers (>20k Daltons).



All experiments done at 0.1 mS/cm as $NaHCO_3$ at 3.5% pulp consistency, pH 7.5

Reference: Sjostrom et al Nordic Pulp Paper Research J, 2000, 15, 5, 469-475.

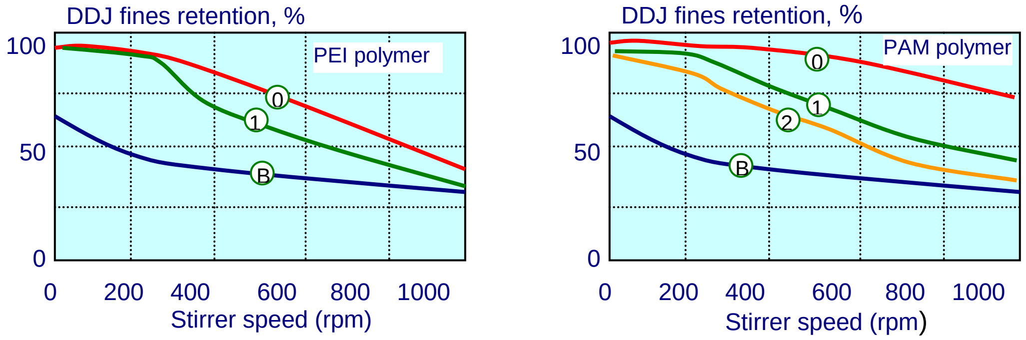
Reflectance

This is an important optical property of papers and is defined as the ratio of the total reflected light from a surface compared to the incident light. Reflectance values are used to calculate the brightness and opacity of paper.

Reflocculation

Aggregates of fine particles have varying floc strengths depending on the nature of the chemicals used to bring about coagulation/flocculation and on the shear levels to which they are exposed. However, flocs that have been broken down by high shear have the ability to re-form once the high shear is reduced, but again this depends on the chemicals used in the first place. Polymers that function by inter-particle bridging (eg polyacrylamides) produce quite strong flocs, but they can be broken down at high shear levels (see example here). This is usually attributed to disruption of adsorption and re-distribution of the polymer into a flatter conformation on the particle surface with reduced bridging potential. By contrast, patch-flocculated suspensions are disrupted at lower shear levels, but the still-present patches can re-associate to re-establish flocculation once the shear is removed.

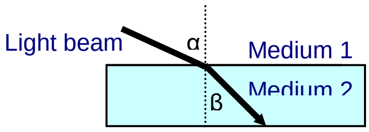
This difference between bridging and charge-patch polymers is illustrated below in a DDJ experiment using a 50:50 bleached hardwood/softwood Kraft pulp with 20% clay filler. The "B" line shows the blank with no added chemicals and the numbers on the other lines refer to the number of times the stock has been subjected to one minute at high (1500 rpm) shear, which is sufficient to break both floc types. It is evident that, once broken, the polyacrylamide flocs have less ability to re-form than the PEI flocs. Similarly, particle aggregation by charge neutralisation produces rather weak flocs, but they are also able to re-form in the absence of the shearing force. Other examples of reflocculation are shown here for colloidal silica with a cationic polyacrylamide and with cationic starch, here for bentonite with a cationic polyacrylamide and here for an anionic polyacrylamide with polyethyleneimine.



Source: Unbehend, Tappi J., 1976, 59, 10, 74-77.

Refractive index

This is a measure of the extent to which the direction of light is bent (refracted) at an interface when it passes from one medium to another, usually in papermaking from air to the paper. Refraction occurs due to the velocity of light being different in different media and the refractive index is a ratio of these two velocities. It is more commonly defined as shown in the diagram at right.



Refractive Index = sin α/sin β

Material	Refractive index
Cellulose	1.53
Water	1.33
Oil/paraffin	1.43
Kaolin clay	1.57
Calcium carbonates	1.58
Talc	1.58
Aluminium hydroxide	1.58
Calcined clay	1.59
UF pigment	1.61
Barium sulphate	1.66
Titanium dioxide	2.6-2.7

When the first medium is air, the refractive index is always greater than unity and the second material is referred to as being optically more dense. A high refractive index increases light scattering and hence the opacity of paper. When the paper is saturated with water or oil, the opacity of the paper is reduced and it becomes somewhat translucent as light is refracted less at the interfaces with fibre or filler. The refractive indices of some papermaking materials are given at left.

Release agent

The term "release" is used in papermaking in the context of overcoming the adhesion forces between two materials. Release agents are thus chemical additives that aid this release process, there being two main applications in papermaking:

- within papermaking to aid the release of the paper web on creping.
  This usually involves the addition of chemicals that are more hydrophobic in character than the adhesive such as emulsified mineral oils, fatty acid esters and polyphosphates.
- as a coating application, usually a silicone, in the manufacture of release papers (eg for the backing to self-adhesive labels).

Repulsive forces

There are a two basic forces that tend to push substances apart within papermaking systems and which work against the various attractive forces:

- electrostatic repulsion between substances with like charges. At the wet end of the paper machine, this is a very important inter-particle force as most particulate solids have a natural negative surface charge or acquire one once they are in the wet end. It is also important to the required stability of coating mixes.
- particle-polymer interactions for surfaces that are hydrophilic or contain adsorbed hydrophilic polymers. This is known as steric stabilisation or colloid protection and, although not usually present at the wet end, it is an important stabilisation mechanism for coating mixtures.

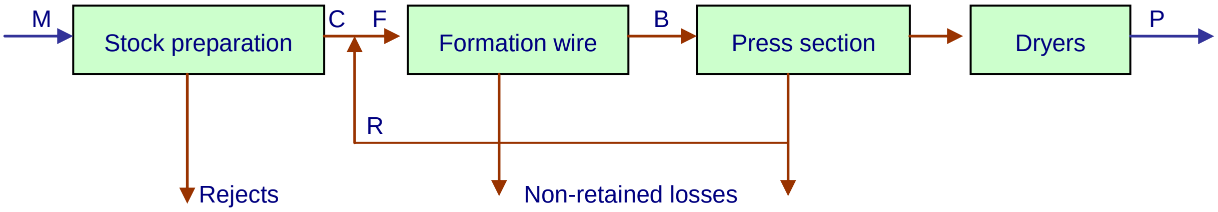
Resin acids

These substances are present in wood as part of the extractives fraction and may thus be present in papermaking pulps depending on their removal during pulping. They are usually measured as part of the pulp's pitch content. Chemically, they are usually described as "diterpenoid mono-carboxylic acid derivatives of alkylated hydrophenanthrenes" and are classified into two groups - the abietic acid type and the pimaric acid type. Rosin size is largely composed of the same acids.

Resistivity

This paper property measures the resistance to the passage of an electric current either along the same side of the paper (surface resistivity in ohms) or between its sides (volume resistivity in ohm.m). It is important for certain electrostatic printing papers where the resistivity is controlled (conductivity enhanced) by size press addition of sodium chloride or a conducting polymer such as a polydadmac. Resistivity is also important for insulating papers, where the retention of even small amounts of electrolytes is undesirable, so the process water supply to such machines is often deionised.

Retention



Total retention based on input raw materials = P/M

Total retention based on cleaned raw materials = P/C

Wire retention = B/F, Press section retention = P/B

Machine retention = single pass retention = P/F = P/(C + R)

The term "retention" is widely used in papermaking to denote the amount or proportion of a material contained in the final product, but there are a number of different retention concepts. In understanding these, it is helpful firstly to define the papermaking system in terms of raw material losses from two distinct areas, stock preparation/cleaning and water removal from the formed paper web (see figure above). As the cleaning losses during stock preparation are deliberate, they should not be included in discussion about retention losses, which are not deliberate, but are inevitable due to the nature of the papermaking process. However, for some raw materials (eg virgin pulps), the cleaning losses should be low and the difference between the original raw material (mass M above) and the cleaned raw material (mass C above) is negligible. For other raw materials (eg recovered papers), the cleaning losses are significant and must be excluded from any discussion of retention.

The total retention is the retention of the overall papermaking system and is the mass of (dry) paper product as a proportion of the total (cleaned) input to the system (usually expressed as a percentage). On the paper machine itself, the mass of material applied to the formation wire is the mass coming from stock preparation plus any material that is returned to the thin stock, notably in recycled waters used for stock dilution and in the returns from any saveall present (mass R above). It is this mass of material applied to the formation wire that is used to calculate the second retention parameter, the single pass retention (SPR).

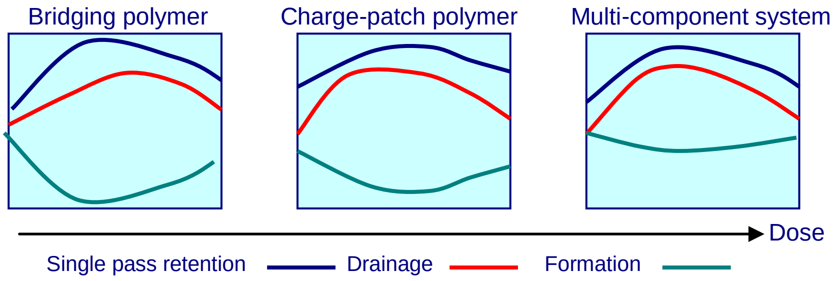
SPR is the fraction or percentage of a material in the paper compared to that at the flowbox. It thus includes retention effects on the wire, in the press section and in the drying section. The term "first pass retention" is often used interchangeably with SPR, but it should only be used for the single pass retention under start-up conditions, ie the first time that the furnish passes the flowbox. The unqualified term single pass retention should be reserved for defining the steady state retention over the whole forming/water removal zone from the flowbox forwards.

Retention aids

These are chemicals added at the wet end to optimise the single pass retention (SPR) of the fine particulate solids in the papermaking furnish. This could be achieved just by maximising particle (floc) size, but this would be very unlikely to satisfy the requirements in two other key areas impacted on by retention chemicals:

- the productivity of the paper machine as influenced by the water removal characteristics of the papermaking stock, particularly its drainage on the formation wire
- the uniformity of the paper, as judged by its formation quality in the x-y plane of the paper.

Good drainage and good formation often tend to go together, but, as shown in the figures below, this does not occur, at least with single chemical treatments, at the same dose as that giving maximum single pass retention. Although the improvement in raw material efficiency (total retention) that accompanies a high single pass retention is important, the range of other benefits (see this list) are of equal or perhaps greater importance. One of these benefits is the even-sidedness (lack of two-sidedness) of the paper. Provided that operation with a high single pass retention is able to produce paper of good formation quality, retention aids have the ability to improve overall paper quality through improving its uniformity in the z-direction as well as maximise productivity and material efficiency.



Different types of aggregating chemical (coagulant and/or flocculant or micro-particle system) tend to be used to achieve these two different effects in the papermaking system, as suggested by the complimentary characteristics of bridging and patch flocculants shown in the table below. Maximum (not necessarily optimum) retention is achieved normally by polymers using the bridging mechanism and hence generating large, loose flocs. This is often accompanied by poor formation, but this is caused not so much by fines aggregation, but by excessive aggregation of the intact fibres. The objective behind the addition of retention (and drainage) aids is to increase aggregation of the fines without unacceptable aggregation of the fibres. Shear levels play a very important role in retention aid performance and this is discussed further under that heading.

Characteristic	Bridging polymers	Charge patch polymers
Floc size	Large	Small
Floc strength	Good	Poor
Floc recovery after shear	Irreversible	Reversible
Retention effect	Good	Moderate
Drainage effect	Moderate	Good
Paper formation	Poor	Good

Retention (and drainage) aids can be classified in several different ways:

- by their aggregation mechanism
    - charge neutralisation with chemicals such as alum and PAC
    - patch flocculation with chemicals such as polydadmacs and polyamines
    - bridging flocculation with chemicals such as polyacrylamides
    - network flocculation with micro-particle systems.
- by their chemical character
    - inorganic chemicals sub-divided into specific chemicals such as
        - alum, which is not used primarily for this purpose, but its presence affects fines aggregation
        - bentonite, one of the two main micro-particle retention chemicals
        - colloidal silica, the other main micro-particle retention chemical
    - organic chemicals sub-divided into specific chemicals such as
        - polyacrylamides, the only retention chemical available in cationic and anionic forms
        - polyamines, one of several cationic charge-patch and charge-neutralising chemicals
        - polydadmacs, one of the other cationic charge-patch and charge-neutralising chemicals
        - polyethyleneimine, perhaps the best-known cationic charge-patch and neutralising chemical
        - polyethyleneoxide, the only nonionic retention chemical
        - cationic starch, which is not used primarily for this purpose, but it affects fines aggregation
        - polyvinylamines, a relatively new type of bridging or charge-patch agent
        - dendrimers, a new category of cationic charge-patch and charge-neutralising chemical.
- by the number of components
    - single component system such as one polymer
    - dual such as [alum + polymer] or [polymer + silica or bentonite]
    - triple such as alum + polymer + silica or bentonite.

The major advance in retention (and drainage) aid chemistry over the last 20 years or so has been the development of multi-component retention aid "systems" having two or maybe three components, which are able to optimise retention, drainage and formation concurrently. These systems sometimes describe themselves as multi-functional in the sense that they are designed to maximise concurrently both retention and drainage and sometimes paper strength as well.

The last effect is often achieved through the retention/drainage aid(s) working with other additives that themselves influence the state of particle aggregation, but which are mainly added for their strengthening effect, eg dry strength additives such as cationic starch and wet strength additives such as the polyamide-polyamine-epichlorhydrin resins. It is obvious that retention aids must be compatible with essential functional additives such as these, but an optimum system could well be achieved by adjusting the functional additive to work with the retention/drainage aid, not solely vice versa.

The other important issue which is best handled within the retention aid system is anionic trash. This is partly because these substances can adversely affect the efficacy of retention aids, but also because the most common way to deal with this set of materials is by the use of chemicals that are already used as part of retention aid systems, notably low molecular mass cationic polymers (eg polydadmacs) or aluminium compounds.

Retrogradation

This is the term for the tendency of starch solutions to "set-back" or form a precipitate on standing. This is caused by inter-molecular hydrogen bonding between amylose molecules, particularly those with a low molecular mass. The cereal starches thus retrograde the most quickly due to their lower chain length and higher amylose content. The most stable starch solutions are produced from the waxy maize starches, as they are close to 100% amylopectin. Most modified starches have a lower retrogradation tendency than native starches as the functional groups thus introduced interfere sterically with the ability to hydrogen bond.

Reversion

This term is used in relation to changes in the properties of paper products in two areas:

- brightness reversion, where there is a loss of brightness in papers containing some mechanical pulp
- size reversion, where the paper is sized at the paper mill, but loses some or all of its sizing over time.

Rheology

This is the science of the deformation and flow of matter, ie how matter responds to the stresses placed on it. The importance of rheology in papermaking is mainly in relation to paper coating due to the high concentrations in the coating mix, but the principles are also relevant at the wet end in terms of suspension uniformity and fibre orientation. Materials can respond in two distinct ways to stresses:

- they can deform elastically (reversibly) and return to their original state when the stress is removed, this being a typical behaviour pattern for solids
- they can deform irreversibly (ie flow), this being a typical behaviour pattern for liquids.

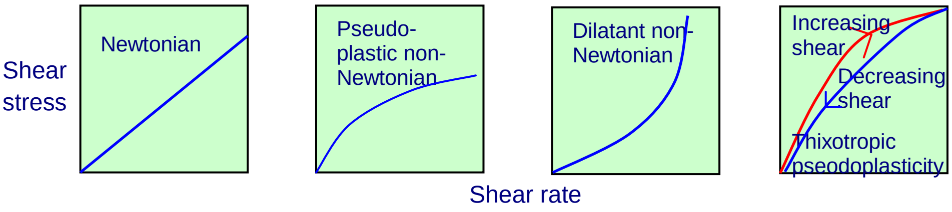
In addition, some materials exhibit both types of deformation and are classified as being visco-elastic.

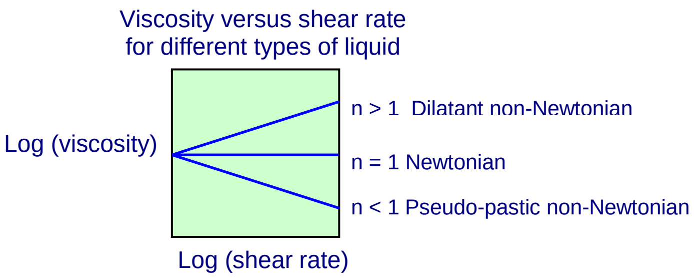
Liquids can be classified as being Newtonian or non-Newtonian depending on the relationship between the shear stress and the shear rate or between its viscosity and the shear rate. Generally, the relationship between shear stress and shear rate for a liquid can be written as a power law:

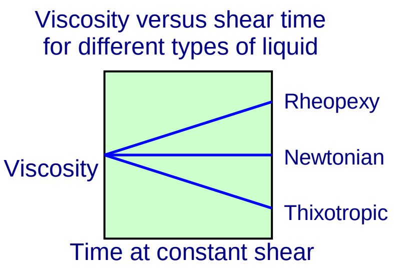
$$\text{Shear stress = constant x shear rate}^{n}$$

There are three main types of liquid behaviour, as shown in the graphs below (sometimes referred to as rheograms). For a Newtonian fluid, the shear stress increases linearly with the shear rate (n = 1 above) and the slope (the constant in the above equation) is simply the viscosity. This is typical of the behaviour for the range of aqueous conditions found at the wet end of the paper machine, at the size press and for some coaters (air knife, rod metering).

Shear rate versus shear stress for different types of liquid

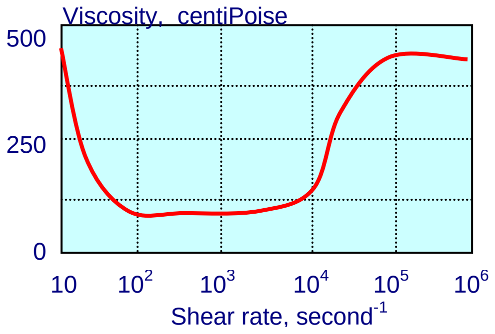






In some conditions such as those found in roll and blade coaters, this simple relationship does not hold and there are various types of non-Newtonian behaviour caused by interactions within and between the particulate and dissolved solids present. Pseudoplastic (shear-thinning) conditions occur where there is an attraction between (often asymmetric) particles in a suspension, but this is gradually overcome as the shear rate increases and the viscosity declines. It can also occur with polymer solutions as the molecules progressively align themselves with the direction of flow. A special case of pseudoplasticity (called just plastic or Bingham plastic conditions) is where there is a minimum stress before flow occurs. Dilatancy (shear-thickening) occurs when a high concentration of particles is packed together as densely as possible with liquid only in the void spaces. In order to flow, the dense packing has to be disturbed, causing the void volume to increase and the limited volume of water, being inadequate to fill the increased void space, causes the suspension to appear to dry out or get thicker. Thixotropic fluids represent a special case applicable to any of these flow conditions where the viscosity change with time depends on the shear history so the shear stress - shear rate pattern depends on the direction of the shear change (as shown in the figure above). The term "rheopexy" is sometimes used to denote time-dependent shear-thickening.

The rheology of a coating mix is defined by its total solids content and by certain characteristics of its main components, notably the particle size distribution of both pigment(s) and insoluble binder(s), the chemistry of any water-soluble binder(s) and the shape and degree of dispersion of the pigment particles, which determine their packing density. A typical rheogram for a coating mixture is shown at right. There is an initial shear-thinning (pseudoplastic) region, during which the weak inter-particle attractions are broken down followed by a period of Newtonian behaviour before a final shear-thickening zone. Coating additives used for other purposes (such as water retention and dispersion) may also influence the coating rheology.



Source: Bown "Review of the influence of pigments on papermaking and coating" Transactions 11th FRS "Fundamentals of papermaking materials" Cambridge, 1997.

Additives may be specifically incorporated in the coating mix in order to control its rheology, notably its viscosity during application. There are two classes of rheology modifier:

- viscosity-reducing chemicals such as dicyandiamide, amines such as diethylenetriamine and polygylcols
- viscosity-increasing chemicals which are usually high molecular weight polymers, often based on acrylates, that are either activated by alkaline conditions (so-called alkali-soluble emulsions) or contain hydrophobic groups that influence their degree of association under high shear. CMC and starches also influence coating rheology.

RMP

This is an abbreviation for refiner mechanical pulp or pulping process.

Rosin

Rosin is used for the wet end sizing of paper, but a second component (normally alum or another aluminium compound such as PAC) is essential for it to work effectively. The use of rosin (with alum) was shown to be an effective sizing agent for paper in the early 19th century and its use grew to the extent that rosin had become the most common wet end sizing agent by the mid 20th century. Following the success of the then newly-developed neutral sizing agents (initially AKD and then ASA) from the 1950s onwards, it might have been predicted that, with the strong trend to neutral papermaking, rosin size would disappear. However, this has not happened, although the use of rosin is certainly much lower today than it once was, particularly in one of the main sizing sectors (wood-free papers). Rosin is still used, albeit in a modified form, to size such papers at neutral as well as acid pH, but, other sectors have become more important and perhaps its largest use today is for the sizing of packaging grades such as linerboard and folding boxboard.

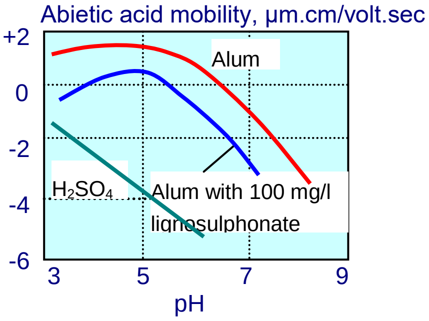
Crude rosin is obtained from softwood trees by three different techniques:

- ❑ gum rosin (oleorosin) by distillation of the exudate of live pines
- ❑ wood rosin by solvent extraction of aged pine stumps
- ❑ tall oil rosin by distillation of tall oil, which is produced by acidification of Kraft pulping liquor.

The most important source of rosin is tall oil, which produces a very pale yellow solid with a softening point of 60-90°C, which is suitable for all paper grades. Rosin is a complex mixture of predominantly (90%) polycyclic resin acids plus a minor fraction (10%) of neutral compounds (resin and fatty acid esters and alcohols). In tall oil rosin, the dominant acids are abietic (35-40%) and dehydroabietic (20-25%) acids with lesser amounts of isopimaric and palustrinic acids (each about 10%). Due to their having several unsaturated carbon - carbon bonds, all the resin acids are chemically reactive and may undergo oxidation, which darkens their colour. The efficiency of natural rosin may be improved by carrying out a simple chemical reaction to produce the so-called fortified sizes and all commercial rosin sizes today contain a proportion of fortified rosin. A more recent innovation in rosin chemistry is the conversion of the acid form to an ester in order to minimise the wet end interaction of ionised rosin with cations, a particular problem when operating at neutral pH levels (see later in this section).

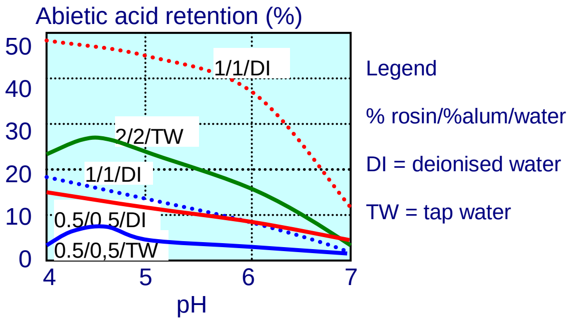
For wet end addition, the rosin has to be converted into a water-soluble or water-dispersible form. The most common type used to be paste sizes, in which the rosin is present as the sodium soap and the solids content is about 75%. However, these were largely displaced by less viscous "liquid" soaps in the form of either the sodium salt with "extenders" such as urea or the potassium salt, both types having solids contents of about 50%. Dry powder rosin soap sizes are also available. However, most rosin sizes used today are rosin dispersions (solids content about 30%) containing at least 80-90% free (natural or fortified) rosin stabilised by the addition of casein (to give an anionic emulsion) or other charged chemicals such as anionic surfactants or cationic polymers. The particle size distribution of the casein-stabilised dispersions is broader and higher (0.5-5μ) than those of the charged dispersions (0.1-0.5μ). A variant of dispersed rosin size is the so-called single-pack or one-shot product, which incorporates the required amount of aluminium compound into the dispersion.

As the pK value of the rosin acids such as abietic is about 5, the addition of soap size to the papermaking stock produces a mixture of unionised and ionised acids, the relative proportions of which change rapidly over the pH range 4.5-5.5. Below pH 4.5, the acid is dominant, whilst above pH 5.5, the ionised form is dominant. This change in rosin form is evident from many studies of the effect of pH on the charge of rosin species (see figure at right where only sulphuric acid is used for pH adjustment). In order to achieve good sizing with rosin, the traditional approach has been to use alum, which can react with the rosin to form positively-charged compounds such as “aluminium dirosinate" (AlR_2^+ where R = rosin molecule) or other polymeric complexes involving olated aluminium species, but the extent of this reaction at the wet end depends on the form of the rosin present and hence on pH (as shown again in the figure at right). Anionic species from pulps (eg lignosulphonate as shown in the above figure) also affect rosin efficiency through their adverse effect on the charge of the alum/rosin complex. Other experiments have confirmed that this effect leads to impaired rosin retention.



Source: Lindstrom in Svensk Papp, 1977, 1, 22-28.

Further laboratory-based studies have shown the impact of pH and water quality on retention of abietic acid (sodium soap form). As seen at right, retention declines progressively above pH 5 at all addition rates, which is due to loss of cationicity of the rosin/alum complex. Electrolytes have also been shown to impair rosin retention at acid pH (due to shielding of the charge attraction between the rosin/alum complex and the fibre), but calcium ions have the biggest impact. When dissolved calcium ions are present, some of the ionised acid is precipitated as the calcium soap and, if excess calcium were present, the equilibrium would eventually convert nearly all the rosin acids to this form. Unfortunately, calcium "rosinates" are not good sizing agents as the precipitated form is not cationic and is therefore poorly retained. This is confirmed in the figure at above right, where the abietic acid retention is lower in tap water than in deionised water.



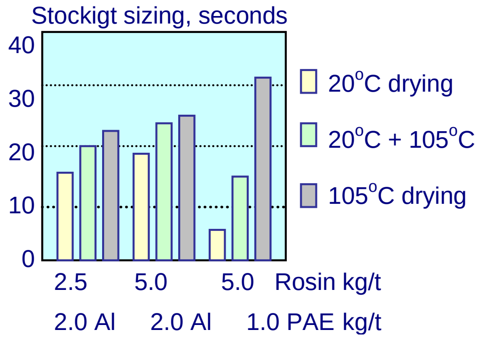
Source: Lindstrom in Svensk Papp, 1984, 3, 2-7.

For the reasons evident in the above figures, rosin soaps have traditionally been used at pH 4.5-5.0 with alum being added to provide both the acidity to lower the pH and as a source of cationic aluminium species. Conventionally, the rosin is added first just before the fan pump followed by alum, but so-called "reverse" sizing (alum followed by rosin) has been used to counter problems when high levels of calcium are present in hard water areas. Although this pH range is below the pK of abietic acid, some direct chemical reaction takes place forming a mixture of aluminium "dirosinate" and the rosin acid. The positive charge on this complex (as seen in the above figure) promotes hetero-aggregation of rosin with particulate solids and reasonable rosin wire retentions. The alum/rosin complex remains cationic once the alum:rosin mole ratio exceeds about 0.25:1 at pH 4.5, but greater quantities of alum would be needed at higher pH levels.

Another important characteristic of rosin soap sizes is the fact that the aluminium "dirosinate"/rosin agglomerate is quite large and tends to get larger as the dose increases. Whilst this is good for rosin retention (as seen in the second figure above), it is less desirable from the standpoint of achieving as uniform as possible a rosin distribution across the fibre surface. As the softening (or sintering) temperature of the aluminium dirosinate is above 120°C, it also cannot redistribute itself in the drying section. For these reasons (reactivity with calcium ions leading to impaired retention and the inability for re-distribution plus the large floc size leading to poor initial distribution), rosin is no longer used in a soap form, but as a rosin dispersion.

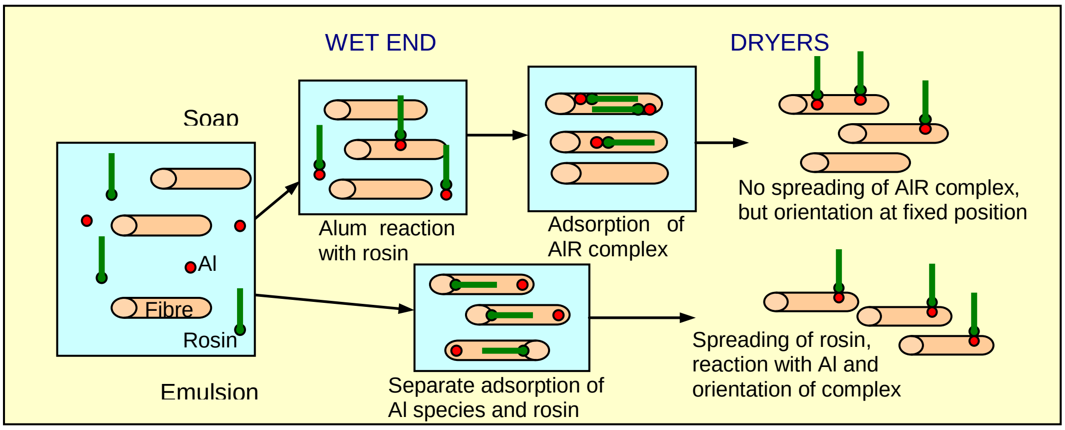
For rosin dispersions, the only chemical reaction taking place at the wet end is reaction of aluminium species with the ionised rosin at the surface of the dispersed particles, a very small fraction of the total rosin present. The emulsified rosin particles are thus retained by a hetero-aggregation mechanism with the rest of the particulates and the aluminium species by adsorption of the cationic complexes onto the whole particulate matrix, not just on the rosin. In contrast to rosin soaps, rosin dispersions form discrete flocs at the wet end and these are more uniformly deposited on the pulp. Furthermore, the rosin emulsion particles are able ultimately to achieve an even better surface coverage as the sheet temperature during sheet drying exceeds their softening temperature (60-90°C), thus allowing the rosin to spread over the whole surface of the particulate matrix.

It is quite difficult to separate the effects of rosin re-distribution from its orientation reaction with alum, but the results shown at right do suggest some temperature dependence in the latter. This work was done with a base paper, which already incorporated the orientation component (alum or a PAE resin), but the rosin emulsion was added by simple impregnation of the dried base paper. The impregnated sheets were pressed to about 60% solids content and then dried in the three ways indicated. It is clear that the sheets exposed to the elevated temperature gave the best sizing and that pre-drying before high temperature drying had little effect.



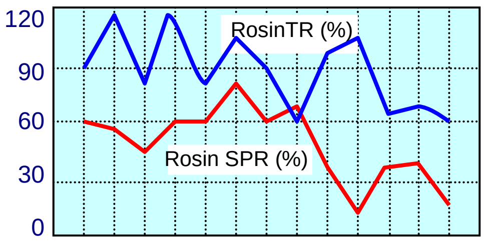
Source: Kitaoka et al in Nordic Pulp PaperResearch J., 2001, 16, 2, 96-100.

From the foregoing, it is clear that the presence of alum is more critical to the retention of soap size than of dispersed size, but its presence is crucial to one other element of rosin performance. Once retained and spread over the fibre surface, the rosin has to be oriented with the hydrophilic part pointing towards and the hydrophobic part away from the fibre surface. For both soap and dispersed rosin sizes, the formation of the “aluminium rosinate” (in the case of the dispersed rosin, through reaction in the drying sheet) anchors the rosin with the optimum orientation. The rosin itself would naturally tend to align its hydrophilic side with the fibre surface, but this is reinforced by the formation of the aluminium salt and any tendency to reverse its alignment in the presence of water is prevented. These differences in the overall mechanism of rosin sizing between the soap and emulsion sizes are summarised in the picture below.



There has been much speculation about the precise form of the active rosin sizing entity in paper and the nature of its association with the fibre surface. This has been probed using extractions with various solvents of sheets "cured" at different temperatures. One school of thought is that there are two different forms of the "aluminium rosinate" material, one forming a strong bond with the fibre surface and the other forming a weak bond. This has been used in place of the melt-flow model of rosin behaviour to explain redistribution effects and the volatilisation of rosin in the drying section. Recent work in Japan using carbon-13 (^{13}C) nuclear magnetic resonance (NMR) of papers sized with with ^{13}C-labelled rosin casts some doubt on the traditional role ascribed to aluminium species as it was difficult to demonstrate the presence of any aluminium salt of rosin. Nevertheless, this same work has confirmed the importance of aluminium species to rosin sizing as papers with zero Al content are completely unsized despite the presence of adequate rosin (0.2-0.3%).

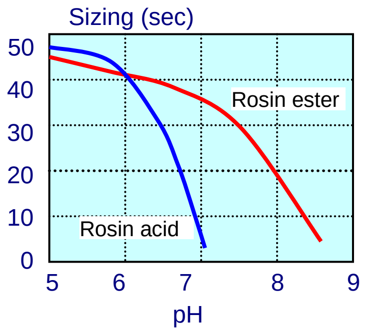
There is very little data on rosin retentions on full-scale paper machines, probably due to the time-consuming nature of rosin analysis (solvent extraction). The data shown below is from a machine making clay-filled papers from a largely bleached hardwood Kraft furnish, but with a wide range in the grammage of its products. The variation in single pass retention of the particulate components was shown here as the first example of the influence of grammage on SPR. The flowbox conductivity on this machine (0.7-0.8 mS/cm) reflected the fresh water baseline (0.3 mS/cm) plus the inputs from the sulphate ions in alum, which was added to give about pH 5 at the flowbox. Dissolved sulphate concentrations paralleled changes in alum addition and covered the range 200-500 mg/l (compared to 30-40 mg/l in the fresh water). Flowbox concentrations of dissolved organics were low (100-200 mg/l) and were mainly derived from starch-containing broke, which had a thick stock COD of 600-700 mg/l.



The single pass retention of rosin was very similar to that of the filler/fines, which is not unexpected as the particle size of the rosin emulsion would have been similar to that of the fines. Single pass retentions of the fines fraction was poor due to inadequate aggregation by the retention aid in use at the time. The total retention of the rosin exceeded 90% for most of the survey period, but dropped dramatically on the low grammage grade, necessitating a significant dose increase in order to maintain the required sizing level. Over the survey period, the machine experienced severe deposition at the press section on the low grammage grade. The deposit comprised rosin (about 20% of the total weight), clay (about 25%) and fibre fines (about 55%), ie those components of the furnish with low wire retentions. The location of the deposit on the second press implied a complex deposition/pick-up/re-deposition mechanism caused primarily by the high flux of poorly-retained material through the machine wire. The solution was to improve the efficiency of the retention aid system and thus raise the single pass retention of the fines at all times, but particularly on the low grammage grade.

As sizes are used extensively in the printings/writings sector, there has been much interest over the last decade or so to size paper at more neutral pH values, thus facilitating its use with calcium carbonate filler. As the wet end pH rises, there are three important effects in a rosin/alum system:

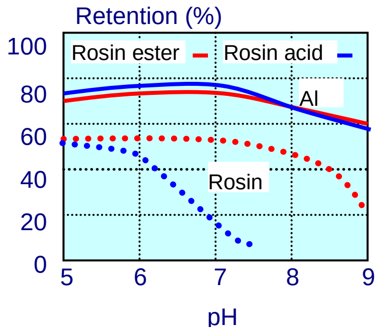
- greater interaction of rosin with calcium and aluminium ions at the wet end due to increased rosin ionisation, thus impairing sizing efficiency through poor wet end distribution and limited re-distribution ability
- the cationicity of any alum/rosin complex declines thus impairing its retention, although this can be compensated for by use of retention aids
- the speciation of the aluminium changes from soluble cationic compounds to insoluble less cationic, nonionic or anionic compounds such as the hydroxide.



Source: Wang in Nordic Pulp Paper Res.J., 2000, 5, 416-421.

For the most effective sizing at neutral pH levels, rosin can be modified chemically to resist ionisation, the best example being conversion to a rosin ester with monohydric alcohols such as iso-octanol or with polyhydric alcohols such as ethylene glycol or glycerol. As well as improvements in sizing efficiency at neutral pH, rosin esters seem to produce more stable emulsions, particularly under alkaline conditions. An example of the benefits of a triglyceride rosin ester is shown at left in the sizing of a bleached hardwood Kraft pulp (refined to 400 ml CSF) at an addition rate of 1% rosin size on pulp for 60 g/m^2 handsheets.

It is evident that the rosin ester emulsion gives much better sizing than the rosin acid emulsion in the neutral pH region and, from the figure at right, that this is due to better retention of the rosin component. There is little difference in the retention of the aluminium component, which is in line with the expected non-reaction between the two components at the wet end. An interesting side avenue of this study looked at the distribution of rosin and aluminium species in the formed paper by scanning electron microscopy. Although the papers had been dried at 105^{o}C for 10 minutes, the distribution of rosin was not that uniform with the fibre surface having obvious bare, uncovered patches. This was also true for the aluminium component, the wet end distribution of which is more important as it does not have the ability to re-distribute itself during drying.



Other techniques to facilitate rosin sizing at neutral pH include:

- delayed addition of rosin (and alum) by minimising contact times at the wet end, this technique also being useful with hot stocks to minimise precipitation of hard aluminium hydroxide deposits
- pre-mixing of rosin and alum which allows some degree of interaction between the two components at a lower pH than that of the papermaking stock.
- use of PAC in place of alum due to its higher and more pH-stable cationicity
- use of cationic rosins that are less dependent on the aluminium component for hetero-aggregation with the rest of the particulate matrix at the wet end.

The performance of all types of rosin size can be adversely affected by various aspects of wet end chemistry. As rosin retention is dependent on a degree of cationic character in the emulsion or the accompanying aluminium component, the presence of anionic trash tends to impair sizing. As well as calcium, inorganic anions (particularly divalent ions such as sulphate, the presence of which is unavoidable with alum) can also impair sizing by lowering the cationicity of the aluminium complexes and the melt-flow characteristics of rosin during drying. Different pulps respond differently to rosin (but no more than they do to all sizes) due to variations in surface area and carboxyl content. High temperatures can be particular problem on machines with closed water systems, but this is more to do with alum than with rosin itself. Increased temperature changes the equilibrium positions of the various alum hydrolysis reactions and seems to make the aluminium complexes less cationic and less stable. A particular problem is the formation of hard deposits of aluminium hydroxide around the addition point, which build up over time and require periodic downtime for removal. High stock temperatures at neutral pH provides a particularly challenging combination of conditions.

Being an amphipathic molecule that is soluble under neutral/alkaline conditions, it is not too surprising that rosin can be implicated in foam problems. However, it is not likely to be the sole cause of the problem unless the rosin retention is poor on a machine with a reasonably closed water system. The resultant high concentrations allied to the elevated temperature could be enough to cause foam either under acid conditions (due possibly to calcium carbonate-generated carbon dioxide) or under neutral conditions (due to formation of the rosin soap).

Depending on machine-specific circumstances (sizing specification, furnish characteristics and wet end chemistry), rosin addition rates vary widely, but are typically 3-5 kg/tonne fibre for wood-free papers. Levels well above 10 kg/tonne fibre may be needed, however, for the more hard-sized grades. Alum doses cover a similar range from 5 to 20 kg/tonne, but much higher doses are sometimes used when alum is (unwisely) added for pH control. One of the disadvantages with rosin sized papers is that they have poor resistance to acidic liquids due to hydrolysis of the aluminium rosinate and subsequent loss of optimum rosin orientation in the paper.

As sizing is intended to modify the surface characteristics of paper, this could have adverse repercussions for paper qualities other than sizing:

- rosin is well-known for promoting adhesion to drying cylinders, which is useful on MG machines to produce a glazed finish, but less desirable if this causes sticking and poor release on rolls and normal drying cylinders.
- rosin has been shown to have a relatively small effect on the frictional properties of paper
- print adhesion (particularly from laser or ink-jet processes) has not been reported to be a problem with rosin-sized papers, unlike some papers sized with other chemicals.

Roughness

This paper property is covered under smoothness.

Runnability

This term is used in papermaking to refer to the multitude of issues that cause the paper machine to run at lower than its intended production rate. This touches on many fundamental aspects of machine design and operation in terms of its overall efficiency and profitability. Machines making the same grade of paper are often ranked in terms of saleable production per unit width (tonne/metre.day or even km^2/metre.day), in which case faster machines tend to be at the top of the list. Under normal trouble-free operation, chemical aspects of the papermaking furnish influence machine speed primarily through their impact on the ease of water removal, notably during the drainage stage on the formation wire. Poor productivity due to unacceptably slow machine speeds could thus be caused by chemical parameters such as a high fines content of the stock, by over-use of wet end starch or by poor efficiency of drainage aids.

A low efficiency level may also result in circumstances where the production rate is acceptable, but the paper quality does not meet the required specification in some way. This may be due to any of a multitude of factors:

- ❑ an incorrect total quantity of retained raw materials leading to a product grammage that is out of specification
- ❑ an incorrect balance of retained raw materials (eg too much or too little filler) in the paper, even though the overall grammage is fine, leading to some key property being outside the specification (eg opacity in the case of filler)
- ❑ sub-optimal distribution of components within the paper, ie poor uniformity in the x, y or z directions
- ❑ inadequate expression of the functionality of a key chemical, eg poor sizing due, possibly, to poor size retention and/or low drying temperatures.

The direct consequence of this is, of course, the generation of machine broke, which may itself impact on runnability through the recycling of materials that might exacerbate the cause of the original problem or create new problems. These new problems may contribute to the most severe type of poor runnability, which is unplanned downtime. This is usually caused by a break of the paper web, often around the press section, but this is just as likely to be due to some sort of mechanical failure or problem as it is to a chemical problem. Most of the chemical issues that cause breaks are due to the set of problematic substances, but there may be other non-specific problems where the surface chemistry of the paper plays an important role, such as unwanted adhesion between the web and machine surfaces (eg fabrics or rolls/cylinders). The wet web strength also plays an important role in runnability around the press section area.

Clearly, process runnability on the paper machine is therefore influenced by many facets of wet end chemistry and, to a lesser degree, by dry end chemistry. Runnability issues are obviously different for surface application techniques, where the quality of the base paper (eg level of sizing) becomes one of the runnability issues.

Sack papers

These are a type of packaging paper that requires not only excellent tensile strength, but also with some extensibility and this is achieved not by the use of chemicals, but by a special creping process which puts an almost invisible crimp into the paper during drying. They are generally made from unbleached Kraft pulp, sized with rosin and additionally treated with wet strength resin when made for use under wet or high humidity conditions.

Salts

This is a general term for inorganic ionic compounds, which are otherwise referred to as electrolytes. The term "salt" is best avoided due to its common usage referring just to sodium chloride.

Sampling

This is important in relation to off-line laboratory analysis and to the location of on-line sensors. For the purpose of giving an overall picture of the system's wet end chemistry, there are four key sampling positions:

- ❑ the fresh water, which establishes the baseline chemistry for the system's soluble components, notably the inorganic fraction. In contrast to components entering with all other raw materials, those entering with fresh water do not build up appreciably as the machine circuit is closed up.
- ❑ the thick stock, which is representative of largely fresh material coming forward to the machine. This can be sampled at different locations, but the best general position is right at the end of the thick stock circuit, directly before the fan pump. If different pulps are being blended, it may be useful to take some samples of the separate streams. Analysis of the broke thick stock can be particularly useful in quantifying the chemical matrix recycled from surface treatments.
- ❑ the thin stock, which represents the whole paper stock at its greatest dilution in the system. differences between the thick and thin stocks will reflect further chemical additions and, most importantly, the dilution with whitewater. Of course, the most important purpose of this sample is for calculation of the single pass retention for particulates.
- ❑ the whitewater, which represents the non-retained constituents of the furnish. This sample can be taken at various specific locations, but the most common are the first tray or the combined tray waters. The first tray position gives the most sensitive indication of retention variations, whilst the combined sample gives a better indication of average losses through the wire. There should be little difference between the soluble components in the thin stock and in the whitewater unless further adsorption/desorption takes place in the whitewater after the bulk of the particulates have been removed.

Other sampling points may be included in order to quantify specific problem areas, eg deposits at critical positions, saveall influent/effluent, press section waters, etc.

It is a commonly-quoted axiom that analytical results are only as good as the representative nature of the sample. Taking the sample and ensuring that its characteristics are preserved prior to the actual analysis is therefore extremely important. Difficulties in representative sampling are related to the heterogeneity of the stream to be sampled (particularly the presence of materials that can separate by settlement or by flotation) and its variable composition with time. The first problem can be largely overcome by ensuring that the sample is taken at a location with adequate shear/mixing to prevent stratification.

From knowledge of the variability in the parameter of interest and the required precision of the result, the number of samples (N) that need be taken can be calculated:

$$N = (k.f.s/p)^2$$

where k = values from the t distribution at the required level of confidence
f = factor dependent on statistic to be estimated
eg f = 1.25 for the median and f = 2.09 for the 95%ile
s = standard deviation, p = precision

This equation assumes that the data is distributed normally, whereas many water parameters are often distributed log-normally. In these cases, the equation has to be applied to the transformed data. The skewed log normal distribution means that there can be occasional very high values which are difficult to predict with any precision. All wet end samples must be analysed as rapidly as possible due to the lability of many of the components, particularly the organic fraction. Refrigeration is the only preservation technique to be used in circumstances where some delay is unavoidable, but this could cause some solubility changes.

Saponify

This is the term for the conversion of a fatty acid from the acid form to a soluble metal soap, as shown below:

$$RCO_2H + NaOH \rightarrow RCO_2Na + H_2O$$

This reaction is important to the production of some rosin sizes and the conversion of acids in the extractives fraction of wood or pulps to a soluble form. The soluble sodium soap may then be re-precipitated through its reaction with dissolved calcium ions at the wet end of the paper machine:

$$2RCO_2Na + Ca^{2+} \rightarrow (RCO_2)_2Ca + 2Na^+$$

This second reaction is undesirable as it converts rosin acids into an ineffective form and may precipitate colloidal pitch.

Satin white

This is a speciality pigment used in paper coating, notably in the manufacture of high-gloss papers such as cast-coated grades. It is made from lime and alum to produce a hydrated calcium aluminium sulphate ($3CaO.Al_2O_3.3CaSO_4.31H_2O$) with needle-like crystals. It can be dispersed with gum arabic.

Saveall

This purpose of this piece of equipment is well described by its name, which is to recover particulate materials (mainly fines) that are neither retained by the papermaking wire nor recycled in the primary loop. The most common treatment units are based on flotation or filtration with many different designs, particularly for the latter. Filtration is carried out without any chemical addition, but chemical flocculation is essential for effective flotation. The recovered solids are returned to the stock preparation system and the clarified water is often re-used on specific applications such as low pressure showers, sealing, hose water, etc.

SB

This is an abbreviation for styrene-butadiene.

SC

This is an abbreviation for super-calendered as in SC papers.

Scale

This is the term for a type of precipitate that occurs in water systems in the form of an adherent film or deposit on the surface of tanks and pipes. Scales are usually inorganic in nature and often grow from a small point of initial nucleation. The most common type of scale in papermaking systems is calcium carbonate, which occurs not through the deposition of calcium carbonate filler, but through its precipitation from unstable calcium bicarbonate. This may be a specific problem in shower (or other) systems using heated fresh water, particularly when the pressure is reduced at the shower head.

The prevention of scales is important in relation to the maintenance of open pipes generally and, in special circumstances such as heat exchangers, in terms of the efficiency of process equipment. The hierarchy of control techniques discussed under deposition is relevant to precipitated scales, additional points relevant only to this type of deposition being:

- ❑ selecting raw materials with the lowest content of components having a precipitation potential

  The most prevalent ion in this category is calcium, but this cation is so widespread that limiting its introduction can be difficult. At some mills, the most significant source of calcium ions is the fresh water and calcium may easily be removed as part of the initial raw water treatment process. The chemistry used to do this depends on whether the calcium is present as temporary hardness or permanent hardness. Alternatively, the anion can be changed from bicarbonate to sulphate by addition of sulphuric acid followed by stripping of the released carbon dioxide. This reduces the water's precipitation potential as calcium sulphate is much more soluble than calcium carbonate. This change may be not be desirable on some paper machines (eg those with closed water systems) due to the activity of sulphate-reducing bacteria or if the mill has an anaerobic wastewater treatment plant. Alternative (but more expensive) acids are hydrochloric and nitric. Scale formation can also be prevented by "conditioning" techniques such as pH adjustment (for calcium carbonate scales) and/or by electromagnetic (or modulating electronic) treatment. Some precipitating anions (eg silicate) are associated with pulps and are best excluded from papermaking by optimised pulp washing.

- ❑ so far as is practicable, optimising machine operation (without chemical addition) to minimise precipitation and scale formation

  As discussed under solubility, the presence of indifferent electrolytes (not having an ion in common with the compound causing the scale) increases the compound's solubility as might an increase in process temperature (but not in the case of calcium carbonate). Neither of these factors can realistically be adjusted to minimise scale formation, but it is important to recognise their influence on scale.

- ❑ dosing of specific control chemicals.

  Chemical treatment to prevent scale formation is possible using various anti-scalants.

SCD

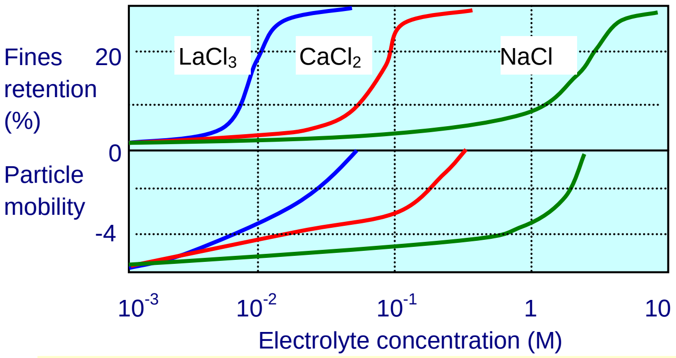
This is an abbreviation for streaming current detector.

Schopper-Riegler (SR)

This is the name given to one of the two standard tests (the other being Canadian Standard Freeness) carried out on pulps to measure their drainage characteristics (freeness) and is used as an indicator of the progress of the pulp refining process.

Schulze-Hardy Rule

This well-known rule applies to the relative effectiveness of electrolytes in promoting particle aggregation. Strictly speaking, this applies only to hydrophobic particles, but it also works reasonably well for many hydrophilic particles. This effect is not due to any specific interaction (eg adsorption) between the electrolyte and the particle surface, but solely due to the impact of the increased ionic strength on the thickness of the electrical double layer. The effective (molar) concentration is proportional to $(1/z)^6$ when the surface charge is high (> 100 mV) and proportional to $(1/z)^2$ when the surface charge is low (< 25 mV), where z is the valency of the counter ion.



Source: Walkush and Williams, Tappi J., 1974, 57, 1, 112-116.

The impact of cations of varying valency is shown in the figure at right in terms of the charge on the pulp surface (measured as mobility of the fines fraction) and the fines retention. In this study on the aggregation of a bleached hardwood Kraft pulp, the optimum (critical coagulant) concentrations for metal chlorides were about 100 mg Na$^+$/l (4.3mM), 13 mg Ca^{2+}/l (0.32mM) and 2 mg La^{3+}/l (0.014mM). This corresponds to a ratio of 100 Na:7.4 Ca:0.32 La on a molar basis. If the Shulze-Hardy Rule applied exactly, these should equate to relative mass concentrations of 100:1.6:0.0013 in the first case and 100:25:11 in the second case for mono-, di and tri-valent cations. The above concentrations for sodium, calcium and lanthanum are somewhere intermediate between these two ratio sets. This difference is probably due to an intermediate surface charge and more specific cellulose interactions with the cations, eg ion exchange with protons or specific ion adsorption, phenomena that do not occur with purely hydrophobic particle surfaces. It should be noted that the type of aggregation brought about by electrolytes is rather weak and would be destroyed by the shear forces on most paper machines. The presence of electrolytes is thus more important in relation to the performance of polymers than what might appear to be a beneficial direct effect on particle aggregation.

Self-sizing

This phenomenon occurs where the paper shows some sizing effect, but without any addition of sizing chemical. This is due to the presence of effective sizing molecules already present in the pulp, the most common source of such agents being the resin acids that are present in virgin wood pulps, notably in mechanical pulps. Self-sizing can also be present in papers made with some unbleached sulphite pulps (notably grades made under acid conditions), but the alkaline nature of the Kraft process usually ensures low levels of resin acids (and pitch) in the pulp. In practice, significant self-sizing is only experienced in wood-containing papers such as newsprint where alum is used at the wet end (not for sizing, but perhaps for pitch control) due to the well-known need for the resin acids (as present in rosin) to be oriented in an optimum manner in order to size efficiently.

Sensitisation

This term has two possible meanings in relation to particle aggregation:

- the involvement of multi-valent ions in forming a link between a polymer and a particle surface that has the same charge, eg calcium ions in the case of the interaction between a negative surface and an anionic polymer.
- the addition of an electrolyte to reduce the thickness of the electrical double layer and hence bring the closest distance of inter-particle approach to within the bridging distance of a polymer.

Sequestrant

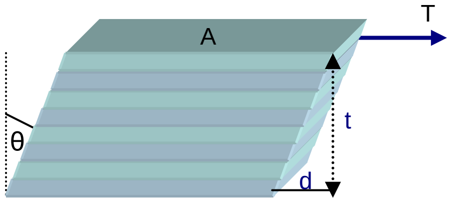
This is an alternative term for chelant.

SGW

This abbreviation stands for stone groundwood pulp or pulping process.

Shear

This concept plays an important role in rheology and is important in papermaking in relation to interactions at both the wet end and in coating mixtures. Shear occurs when one part of a liquid is moved relative to another part by the application of a force, as shown below for a force (T) acting on one side of a volume of liquid.



Shear = d/t, Shear stress = T/A,

Shear strain = θ, Shear rate = dθ/dt

Rigidity modulus = T/Aθ

Viscosity = shear stress/shear rate

Shear is the relative displacement of any two fluid layers divided by the separation distance, whereas the shear rate is the rate of change of the shear with time and thus has the units of time^{-1}. As this is the same as the separation velocity divided by the separation distance, it is also known as the velocity gradient, which is often given the abbreviation, G. An approximate value of the shear rate can be calculated from the power input to the mixing volume as follows:

$$G\ (\text{second}^{-1}) = 1000(E/\eta)^{0.5}$$

where E = power input per unit volume (kW/m^3) and η = dynamic viscosity (cP)

The importance of shear at the wet end and in coating is very different because of the enormous difference in consistencies between them. At the wet end, the liquid suspension behaves as a Newtonian fluid and shear is important in relation to:

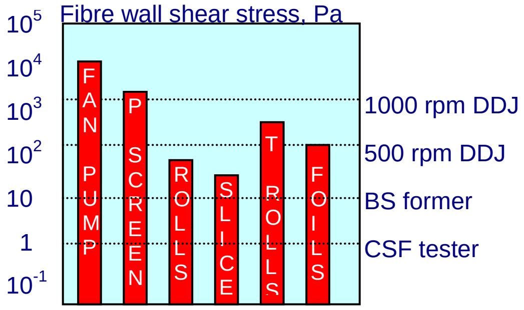
- the uniform mixing of chemical additives with the papermaking stock
- the collision frequency between different particles and between particles and dissolved molecules, as this leads to particle aggregation and adsorption respectively
- the size of flocculated particles, as this is dependent on the strength of the flocculated structure in relation to the applied shear forces.

During the application phase of coating, the liquid suspension may exhibit Newtonian behaviour with air knife and rod coaters or non-Newtonian behaviour with roll and blade coaters. It is important to understand the relationship between the shear level at the coater and the flow properties of the suspension as this will determine the quality of the coating.

The approximate shear rates in different parts of the papermaking system have been calculated as follows:

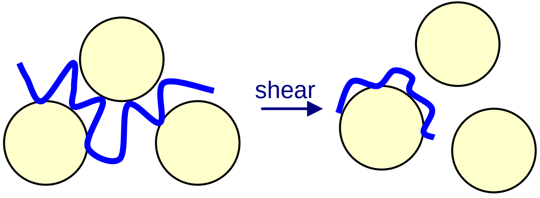
- 3000-4000 second^{-1} at the fan pump
- 2000 second^{-1} at the pressure screen
- 200 second^{-1} at the flowbox slice for a machine speed of 300 m/minute increasing to 700 second^{-1} at a machine speed of 1000 m/minute
- 400 second^{-1} at the rectifier roll on the formation wire for a machine speed of 300 m/minute increasing to 1000 second^{-1} at a machine speed of 1000 m/minute
- up to 10^6 second^{-1} during coating, albeit for a very short duration (micro-seconds).

The impact of hydrodynamic shear on particle aggregation depends on the floc strength compared to the shear-induced stress at the fibre wall (see right for calculated values of this parameter at different machine locations compared to the shear levels in various laboratory systems). For polymeric retention aids, it has generally been found that floc strength increases with the amount of adsorbed polymer and with the polymer chain length and decreases with polymer cationicity (due to lower adsorption). A comparison of the retention levels at various DDJ stirrer speeds (shear levels) for various chemical treatments is shown here.



Calculated for machine speed = 760 m/minute
Source: J.Pulp Paper Science, 1984, July 80-88.

The overall effect of shear on particle retention is also dependent on the ability of the shear-deflocculated suspension to re-flocculate. As shown in the figure below at right, high shear leads to a disruption of inter-particle bridging and a re-distribution of the polymer into a flatter conformation on the particle surface with reduced bridging potential. By contrast, patch-flocculated suspensions are disrupted at lower shear levels, but the still-present patches can re-associate to re-establish flocculation once the shear is removed. Thus, although the flocculation produced by patch-type polymers is inherently weaker, their flocculating ability can be re-harnessed on the next pass. Similarly, particle aggregation by charge neutralisation produces rather weak flocs, but they are also able to re-form in the absence of the shearing force.



This improved shear resistance of flocs generated by dual chemical treatment is one of their main practical advantages. An example of such a system is a cationic polymer followed by an anionic polyacrylamide, in which the mechanism is a mixture of charge neutralisation/patching and inter-particle bridging. The strength of the floc is attributed to the strong electrostatic interaction between the two oppositely-charged polymers. As it is critical that this interaction takes place between the adsorbed, not the dissolved, cationic polymer and the added anionic polymer, there must be adequate time between the dosing points for this to take place. This usually means adding the cationic polymer around the fan pump on the paper machine - the precise position before or after the fan pump depends on the amount of shear required to optimise the primary state of aggregation and the time required to achieve optimum conformation of the adsorbed polymer. The anionic polymer is then added before or after the screen, again depending on the amount of shear required to achieve the desired final state of aggregation. Because a bridging polymer is used as the final treatment, such systems can easily lead to poor formation in the product. The desire to combine good fines single pass retention with good paper formation led to the development of the so-called “micro-particle” chemistries based typically on the use of either colloidal silica or bentonite.

Shives

This is a term for over-sized fibre bundles that have not been fully separated in pulping processes.

Silicon

This is the second Group 14 element in the Periodic Table with an atomic mass of 28. Silicon is extremely abundant naturally either as silica (eg quartz) or numerous silicate minerals. Silicon is a fairly common element within papermaking in the following forms:

- ❑ as inorganic silica compounds either as silica or, more commonly, as combined silicates
- ❑ as organosilicon compounds (silicones) for use to control foam and as a release agent.

Silica

Silica is silicon dioxide, SiO_2, which has several applications in papermaking:

- ❑ as nano-particle sized colloidal silica for use as a retention and drainage aid
- ❑ as micro-particle sized amorphous silica powder, which is used for various applications:
    - as a defoaming agent (after surface-treatment)
    - as a speciality wet end opacifier (filler)
    - as a size press additive to improve ink receptivity, notably for ink-jet printing papers
    - as a size press additive to increase surface friction.
    - as a coating additive, notably as the pigment (with polyvinylalcohol) in the special coating applied to the highest quality papers used for ink-jet printing.

For both types if silica, the suspensions are characterised by the pH-dependent ionisation of silanol (Si-OH) groups to give an anionic surface. The amorphous silica products are made by precipitation and are thus sometimes referred to as precipitated silica or precipitated synthetic silicates. In some products, aluminium oxide is co-precipitated to give synthetic alumino-silicates. Many of their applications stem from their high porosity, which provides rapid take-up and immobilisation of the liquid phase in inks, thereby improving ink hold-out. Oil absorption is up to about 3x the silica mass. As synthetic pigments, they all have a high brightness (>93% ISO) and high light-scattering coefficient (around 450 m^2/kg) although their refractive index is similar to that of other fillers (about 1.5).

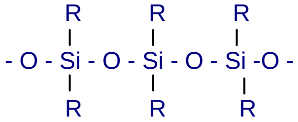
Silicates

Silicates are the most abundant naturally-occurring minerals and are generally based on the tetrahedral SiO_4^{4-} unit as in the very weak orthosilicic acid (H_4SiO_4). There are two broad categories of silicates that find applications in papermaking:

- ❑ in an insoluble form as various clays
    - with alumina to form the general class of alumino-silica minerals such as kaolin clays and some synthetic pigments
    - with magnesia to form magnesia-silica minerals such as talc
    - with alumina and magnesia to form the bentonite clays
- ❑ as soluble silicates, notably sodium silicate.

Silicones

These chemicals are mainly used as defoamers and as release agents, eg for baking papers and for the backing paper to self-adhesive labels. They are a type of organo-silicon compound with the generic structure shown at right. The alkyl (R) group is usually a methyl group, which gives the polymer chain its hydrophobic character, but other groups can be incorporated to give different release characteristics, eg higher alkyl groups for easier release. The liquid silicone has to be cross-linked to give a hard surface layer, there being two main types of cross-linking reaction:



$$-O-\underset{\underset{\displaystyle R}{|}}{\overset{\overset{\displaystyle R}{|}}{Si}}-O-\underset{\underset{\displaystyle R}{|}}{\overset{\overset{\displaystyle R}{|}}{Si}}-O-\underset{\underset{\displaystyle R}{|}}{\overset{\overset{\displaystyle R}{|}}{Si}}-O-$$

- tin-catalysed condensation or platinum-catalysed reaction between the silicone and an Si-H group
- radiation-cured processes using ultra-violet light or an electron beam.

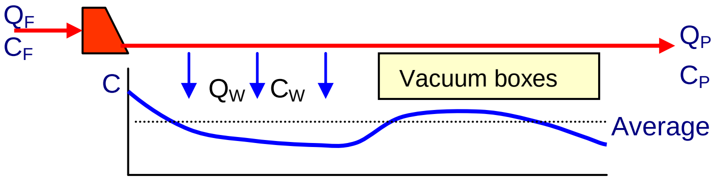
The silicones are applied as solvent-based products or emulsions using normal coating equipment.

Single pass retention (SPR)

This is the fraction or percentage of a material in the paper compared to that at the flowbox (see here for comparison with meaning of total retention). It thus includes retention effects on the wire, in the press section and in the drying section. The term "first pass retention" is often used interchangeably with single pass retention whereas it should only be used for the single pass retention under start-up conditions, ie the first time that the furnish passes the flowbox. The unqualified term "single pass retention" should be reserved for defining the steady state retention from the flowbox to the final reel. In discussing single pass retention, it is essential to consider the effects of each of the three water removal processes (drainage, pressing and drying) on each of the two bulk phases present – the dissolved solids and the particulate solids.

The single pass retention of the total particulate solids (sometimes referred to as "total SPR") is complex and, on any paper machine running under fixed conditions of wire design, speed and product grammage, the single pass retention on the wire part is largely dependent on the state of particle aggregation and this is controlled by the use of retention aids. Particulate retention in the press section is close to 100%, but depends on the integrity of the paper's wire and top sides in relation to the adhesive forces between them and press rolls/felts. Although much of the particulate matrix is immobilised by the time that the web reaches the press section, the fines can still re-distribute itself as shown in this example. In the drying section, particulate retention is even closer to 100% due to the stronger surface bonding at the prevailing higher web dryness.

Retention on the wire is thus the dominant component within the overall single pass retention, which is normally calculated from measurements of the flowbox and whitewater consistencies as illustrated at right. It should be noted that the particulate retentions within the pressing and drying sections are assumed to be 100% in this calculation. This picture shows a typical concentration profile down the wire, the concentration dropping in line with the improved filtration before suffering a reversal when the web experiences the stronger dewatering forces at the vacuum boxes. The single pass retention of any particulate



$$\text{Single pass retention} = M_P/M_F = Q_P.C_P/Q_F.C_F$$
$$= (Q_F.C_F - Q_W.C_W)/Q_F.C_F$$
$$= 1 - (Q_W.C_W/Q_F.C_F)$$
$$= 1 - (C_W/C_F) \text{ as } Q_W \sim Q_F$$

component can be measured in the way illustrated, but it is normally only done for the total particulate solids (consistency) and its ash component.

By contrast, the single pass retention of dissolved solids cannot be estimated from concentrations, as these should be the same (or very similar) in the flowbox stock and whitewater. Unless they are adsorbed by the particulate matrix, wet end dissolved solids follow the water as it is expressed from the web during drainage and pressing and then, with the exception of any volatile compounds, remain behind in the sheet as the water is evaporated in the drying section.

Assuming that the retention of particulate solids is 80% on the formation fabric and that the particulate consistency is 1% at the flowbox and 15% at the couch, then the wire retention of dissolved solids is 5.3%. Assuming that the solids content is 40% at the entrance to the drying section and that the retention of particulate solids is 100% in the press and drying sections, then the retention of dissolved solids is 18.9% in the press section and 100% in the drying section. The overall SPR of dissolved solids can be calculated to be 1.2% under these conditions. This value will vary with the precise conditions, but is always somewhere in the region of 1%.

Overall, the wet end furnish can usefully be sub-divided into three groups on the basis of their different retention mechanisms:

- materials with high single pass retention (>90%)

  The main set of materials in this group are genuine fibres, which are well retained without any help from other additives simply by the normal sieving mechanism on the wire. Because of this, their SPR is little affected by process variables such as grammage or retention aid chemistry. It should be emphasised that "fibres" in the sense used here are not the total pulp particulate solids, but that fraction retained on the 200 mesh screen used in the standard test for fines content. Clearly, the SPR of the pulp's fibre fraction is influenced to some degree by the mesh size of the papermaking wire, but it is normally found that the single pass retention of this fraction is at least 95%. Well-aggregated fines can also have retentions in this range, but the fibre fraction would then probably tend to be over-flocculated and result in poor paper formation.

- materials with intermediate single pass retention (10-90%)

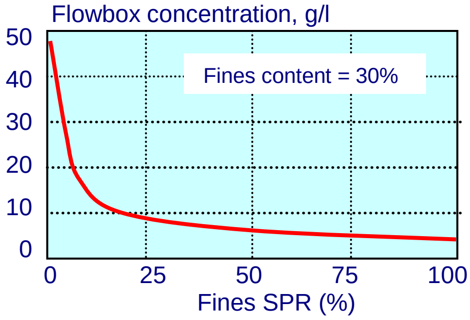
  This covers a wide range of particulate materials extending downwards in particle size from pulp fines (ie those passing through 200 mesh wire) into the colloidal size range and including, where present, fillers and size emulsions. The natural SPR of this group of materials is low, but their SPR can be raised towards the value for genuine fibres by chemical addition to promote hetero-aggregation with or deposition onto fibres or homo-aggregation with one another. The SPR of this set of materials (particularly when they are poorly aggregated) is affected by many process variables such as the product grammage, the speed of the paper machine in terms of shear, etc.

- materials with low natural single pass retention (<10%)

  Although some particulate fines can, under certain circumstances (eg poor state of aggregation and/or low grammage), have SPR values below 10%, this group mainly comprises the dissolved solids present at the flowbox. It is useful to sub-divide dissolved solids into chemicals that are purposely added to the wet end (eg cationic starch, wet strength resins, dyes, etc) and those that dissolve from virgin pulps (mainly hemi-celluloses and lignin compounds) and from recovered paper and broke (mainly starches). Once dissolved, this second group of materials is unlikely to be re-adsorbed by particulates without special chemical treatment and their SPR will be close to that of the liquid phase, ie around 1% as described above.

The overall single pass retention of water-soluble chemical additives is complex as it depends on their distribution amongst the above three fractions. Such additives are selected in the first place on the basis of their good adsorption characteristics so the amount of additive that remains dissolved at the flowbox should be low. The SPR of the additive will then be mainly influenced by the relative proportions adsorbed on genuine fibres (inherently high SPR) and on fines (variable SPR depending on the level of flocculation achieved). As the available surface area is a key factor determining the extent of adsorption, a significant proportion of any additive is normally taken up by the fines and hence the fines SPR is the most important factor determining the additive's overall SPR and total retention (see this calculated model example).

In this figure, the relationship between total fines retention and fines SPR is shown. The SPR of a material is one of its most important attributes in terms of wet end chemistry as it determines its equilibrium concentration at any particular level of water closure, which in turn influences a whole range of wet end effects. This is shown in the figure at right, from which it is evident that, when the fines SPR is below about 20%, the flowbox consistency enters a region (consistency > 1%) where, for most paper grades, it is not possible to make paper and maintain acceptable quality.



It should be evident from the above discussion that, whilst the single pass retention of the dissolved solids is often ignored, it is quite straightforward to calculate based on the water balance from the flowbox forwards. The opposite situation applies to the single pass retention of the particulate fraction, which is recognised as being of great importance and is therefore calculated on most paper machines from measured consistencies. However, it is a very complex parameter as it is influenced by many parameters:

- the composition of the thick stock in terms of the fibre:fines balance (see this example for the effect of fines content on total SPR)
- by the interactions between the particulate matrix and other wet end additives
- by the wet end hydrodynamics and shear forces, which influence inter-particle aggregation
- by the quality of the paper such as grammage.

Whilst reducing losses is one of the main driving forces for maximising single pass retention, it is certainly not the only one and there are other substantial benefits to be gained:

- more stable SPR (see these figures in terms of reduced SPR variability at high SPR levels) leading to improved product uniformity and the production of less broke, which in turn would reduce the recycling of poorly-retained dissolved solids from any size press additives
- a lower flowbox consistency (as shown in the example above in this section) due to reduced recycling of non-retained solids in the whitewater leading to better paper formation/strength
- a cleaner system, as there are lower levels of potentially deposit-forming recycled solids, leading to fewer breaks and lower costs for deposit control
- more uniform paper quality due to the more even z-distribution (less 2-sidedness)
- better efficiency of chemicals that are associated with the fine particulate fraction
- greater degree of water closure possible before encountering problems related to the build up in the concentration of particulate solids, leading to improved solubles retention
- faster equilibration at grade changes leading to less broke at start-up.

Size

This is shorthand for sizing agent.

Size press

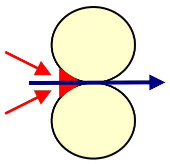
This piece of equipment is a type of roll applicator (as used sometimes as a genuine coater), which is used to apply a solution of chemicals to the dried paper surface. The most common application is starch addition to improve the surface strength of the paper or board, but other chemicals such as sizing chemicals, fluorescent brightener and even pigments may also be applied to give other specific effects. Size press solutions may also contain process additives to control problems such as microbial activity and foam. The size press is used on most machines making wood-free printing/writing papers (including coated grades) and some packaging grades (eg fluting medium).

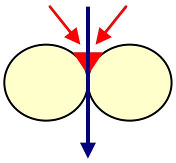
Because of the high concentration of size press solutions (typically around 10% total solids content), it is important to ensure the chemical compatibility of all components when formulating a size press solution that contains more than just starch. Otherwise, this can lead to chemical inactivation of some additives (eg of brighteners and sizes through charge effects) and possible precipitation, deposition and poor runnability. Because the size press solution has a recirculation system, it is possible that water-soluble substances (eg ions and anionic trash) will be extracted from the paper web by the hot conditions in the size press and build up in the size press solution. This is most likely to be an issue on machines with high inputs of water-soluble substances at the wet end combined with quite closed water systems (ie recycled fluting and liner).

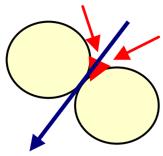
There are three different configurations for the conventional "puddle" size press as shown below, but all function by allowing the paper web to imbibe the applied solution during its short residence time in the press nip. The inclined size press is a compromise between the ease of web run, but unequal pond volume (and hence pick-up) of the vertical size press and the more tortuous web run, but equal pond volume, of the horizontal size press. In all cases, one roll is hard (metal surface), whilst the other is soft (rubber surface) and one roll is fixed, whilst the position of the other can be adjusted to vary the nip pressure.

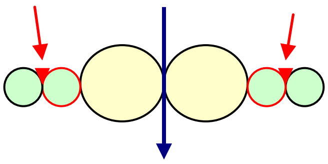
The applied solution is supplied by pipes running across the web so that the solution is fed into the two nips to form a small pond or puddle. The pick-up of solids depends on a number of factors:

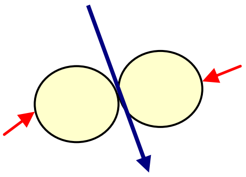
- sizing solution characteristics such as solids content and viscosity
- web characteristics such as grammage, porosity, degree of sizing and moisture content
- machine characteristics such as speed, nip pressure and pond depth.


Vertical


Horizontal


Inclined


Gate roll


Film/metered

The size press-treated paper web can contain 30-40% added moisture, so the size press has to be followed by a set of after-dyers to re-dry the paper. Because of the reduction in production capacity for a given total drying capacity and because of the associated energy costs, there is an interest in replacing size press addition with wet end addition where this is practicable - one example is the use of wet end cationic starch in place of size press starch in the manufacture of recycled fluting.

This change of addition point is also relevant to faster machines where splashing and film-splitting give inconsistent pick-up, but this can partly be overcome by changing to an offset pond arrangement as in the gate roll size press shown above. Other, more modern designs of size press are based on coater designs such as rod or blade metering devices. These are sometimes referred to as short-dwell applicators, film presses or metering size presses (see above). One of their advantages is the ability to use starch solutions of higher viscosity and solids content, thus reducing water pick-up at the same starch pick-up and increasing production capacity. These newer designs are also being used to improve the paper surface by incorporating coating pigments, this being commonly referred to as machine finished pigmentising (rather than coating).

Like coated papers, size press-treated papers have an important influence on wet end chemistry due to the dissolution of the size press-added chemicals from machine broke. On some machines (eg those using virgin pulp), the dissolution of size press chemicals will be the main contribution to dissolved solids at the wet end. As starch is the most common size press chemical and is often added at a level of about 5% of the paper weight, the recycling of broke containing any size press starch has a significant impact on wet end microbiological problems and, if the starch has any anionic character (eg oxidised starches), also on anionic trash. High levels of size press-added fluorescent brightener can also make a significant contribution to anionic trash.

Size reversion

This term is sometimes used interchangeably with the term fugitive sizing to describe the situation where a paper that is fully sized at the mill is found to have lost some or all of its sizing at a later time (see here for pictorial representation). Size reversion is sometimes differentiated from fugitive sizing by defining it as the partial loss of sizing over a defined period after which the sizing level remains constant. This has been an issue mainly with AKD-sized papers, where there is the complicating factor that the paper may not be fully sized at the reel. The supposed loss of sizing is then being judged by comparison with an artificially-cured sample, whereas the paper may never have achieved this sizing level in the first place due to some problem with the initial sizing level.

The occurrence of size reversion with rosin-sized papers is rare, but can occur where the rosin is poorly anchored to the fibre and the paper is then exposed to conditions of high moisture. In such situations, the rosin molecule can re-orientate itself with a consequent loss of sizing. This would most probably be caused by an inadequate content of aluminium species (due to inadequate alum/PAC dosing and/or poor retention), as these act as the anchoring link between rosin and the fibre surface.

The main problem of sizing loss over time has been experienced with AKD-sized papers, notably those made with PCC filler (see here for an example). A clear explanation for this effect is hindered by uncertainties about the precise mechanism of AKD sizing, but there are two main hypotheses:

- ❑ the latent alkalinity in the PCC encourages hydrolysis of the various AKD fractions (bound, unbound and possibly that reacted with the calcium carbonate as the salt of the β-keto-acid) to destroy its sizing. This is supported by the fact that reducing the PCC's soluble alkalinity does reduce the hydrolysis reaction.
- ❑ the AKD migrates into the internal pore structure present in the scalanohedral PCC, with which this effect is most commonly observed.

For sizes with an alkene group (alkenyl KDs and ASA), there is one additional reversion mechanism and this is auto-oxidation by atmospheric oxygen whereby the sizing molecule becomes less hydrophobic through the introduction of oxygen-containing groups.

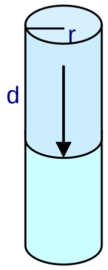
Sizing

Sizing is the process of modifying the surface characteristics of individual fibres or of the formed sheet to resist penetration by a particular liquid. Sizing is carried out for two possible reasons:

- to control the pick-up of aqueous fluids, most commonly starch solutions, at the size press on the paper machine and/or
- to control the penetration of fluids, such as aqueous inks for printing papers or aqueous beverages for liquid packaging papers, during use of the paper.

Sizing is thus mainly applied to printing/writing (and copying) grades and to many packaging grades. Sizing is not commonly applied to wood-containing printing papers, but virtually all wood-free printing papers are sized. It should be noted that, when looking at the degree of sizing brought about by different chemical treatments, some pulps (mainly virgin mechanical pulps) possess a degree of "self-sizing" due to the presence of resin/fatty acids in the pulp, so less additional sizing agent may be required for the sizing of papers containing such pulps.

The relationship between the penetration of a fluid into a porous substrate like paper is given by the Lucas-Washburn equation (see right for the situation in the absence of any applied pressure). Fluid penetration into paper depends on its ability to wet and spread across the substrate and this is primarily dependent on the contact angle, but the paper's capillary structure is also important. Although measurement of the contact angle can be used to assess the degree of sizing, simpler techniques are usually preferred. The main techniques are penetration tests, the results from which are dependent on the fibres' hydrophobic character and on the paper's pore structure, both at and beneath its surface. The two most common tests are the Cobb test and the Hercules size test (HST).



$$d^2 = \frac{r.\ t.\ \gamma.\ \cos\theta}{2\eta}$$

where d = penetration after time t
r = capillary radius
γ = interfacial energy water-paper
θ = contact angle
η = viscosity of water

In accordance with the above equation, penetration of a fluid into the body of paper can thus be restricted by two techniques:

- closing off the surface with a film-forming chemical, thus arresting capillary action. This technique is harnessed in the application of starch at the size press, but, in practice, this is more for improving strength properties than for reducing water pick-up. This technique is obviously only possible when the machine has some form of surface applicator.
- the addition of chemicals to increase the contact angle. In the case of water, this involves the addition of partially hydrophobic chemicals to reduce the paper's surface energy. These chemicals are always amphipathic as they must not only have some hydrophobic character to resist water, but also some hydrophilic character to orient themselves in the optimum way in the paper. These chemicals may be added at the wet end or to the surface of the formed paper. The other type of sizing in papermaking is for oil/grease resistance, which involves the addition of oleophobic (hydrophilic) compounds such as fluorochemicals to enhance the natural oleophobic character of cellulose. This is mainly done by surface application.

The contacting fluid against which the size is attempting to protect the paper may be an ink in the case of printing papers or a beverage in the case of papers/boards for liquid packaging. It is obvious that the sizing agent must be chemically stable under these conditions, otherwise the sizing effect will disappear on prolonged contact. The main consideration for sizing against aqueous fluids is the size's resistance to hydrolysis by aqueous phases that are either slightly acidic or slightly alkaline.

Sizing agent, surface

These are hydrophobic chemicals that are added directly to the dried paper surface, but it is quite common for a surface size to be applied to a paper already sized at the wet end. Surface sizing is chiefly done at the size press, but it may also be carried out at the water boxes on machines equipped with calenders. There are three main reasons for surface (as opposed to wet end) sizing:

- to provide sizing where wet end addition is difficult due to poor size retention caused by , for example, interference effects on machines with closed water systems (eg recycled liner)
- to overcome the tendency for starch addition at the size press to reduce the sizing level achieved by wet end addition
- to improve the surface characteristics for particular paper grades, eg better water resistance of papers used for ink jet printing or better barrier properties for packaging grades.

The chemicals used for surface sizing can be divided into two broad categories:

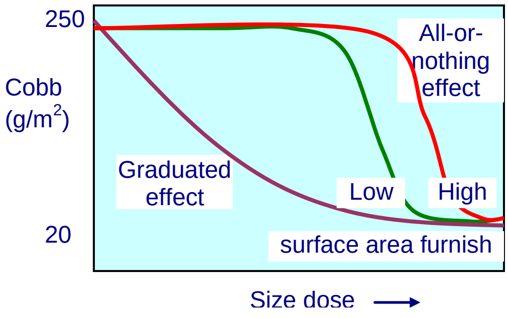
- variants of sizing agents that are also used at the wet end
    - rosin, although this is not commonly added at the surface
    - alkylketene dimer (AKD), which can be used at the size press with normal size press starches when formulated as an anionic dispersion (rather than its normal cationic form).

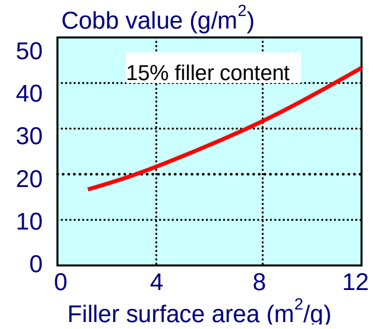
- sizing agents specifically developed for surface application, notably those designated as so-called polymeric sizes. There are two distinct categories:
    - the family of products that are co-polymers of a hydrophobic component (styrene, acrylate esters and methacrylate esters) and a hydrophilic component based on acrylic/maleic acids or their derivatives. The number and balance of hydrophobic and hydrophilic groups determines whether the product is an aqueous solution or dispersion. This gives rise to the styrene-acrylate ester sizes, the styrene-acrylic acid sizes and the styrene-maleic anhydride sizes and the acrylate sizes.
    - the polyurethane sizes supplied as colloidal dispersions.

The polymeric sizes can be made either by solution polymerisation or by emulsion polymerisation (as for coating latices). The solution polymers have been largely superseded by the dispersion/emulsion polymers because of their superior sizing performance, which is due to a combination of higher molecular weight and greater hydrophobicity and the absence of problems such as foam and instability induced by the presence of electrolytes and changes in pH.

Sizing agents, wet end

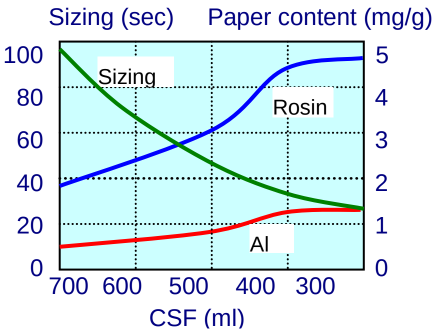
Sizing at the wet end (also called internal sizing) is carried out by the addition of hydrophobic chemicals prior to web formation, although actual sizing is not achieved until the paper has been fully dried. It is not uncommon, particularly for wood-free printing grades, for further sizing also to be carried out by surface application. Most wet end sizes have a sizing-response curve similar to the two upper lines in the figure at right. This "all-or-nothing" effect occurs because of the need to cover all the exposed fibre surfaces before effective water resistance is achieved, otherwise water is wicked in through the uncovered fibre surfaces.





Source: Bown in "Paper Chemistry", Blackie, 1996, Chapter 11, 194-230.

As shown in the above figure, the dose of sizing agent required to achieve a particular level of sizing depends on the surface area of the furnish. This effect is illustrated in the two examples shown here. The first example (at left) illustrates the case where the surface area of the furnish was changed by using calcium carbonates of different particle size and hence of different specific surface area. The paper was made from a bleached Kraft pulp and sized at a constant dose of alkyl ketene dimer.



Source: Wang in Nordic Pulp Paper Res.J., 2000.15, 416-421.

The second example (at right) illustrates the case where the surface area was increased by refining the pulp (bleached hardwood Kraft) and then sized with rosin/alum. Despite the increased retention of both rosin and aluminium species, the sizing level (Stockigt method used in Japan) declined as the refining level was raised. This increased retention of rosin is similar to the increased filler retention that accompanies pulp refining in the absence of retention aids (see this example here).

For effective sizing, the most important requirements are that the size chemical must be well retained in the sheet and the molecule must be oriented in the optimum way with the hydrophobic part of the amphipathic size molecule pointing away from the fibre. All wet end sizing agents are added as fine emulsions or dispersions, which become part of the particulate fines fraction. Their single pass retention is therefore intimately connected with the single pass retention of pulp fines and filler (see this example for AKD). The largest category of wet end sized papers is wood-free printings/writings, which is a large user of fillers, so the interaction with filler, as well as fibre, surfaces is another important facet of sizing (as shown in the example directly above in terms of filler content).

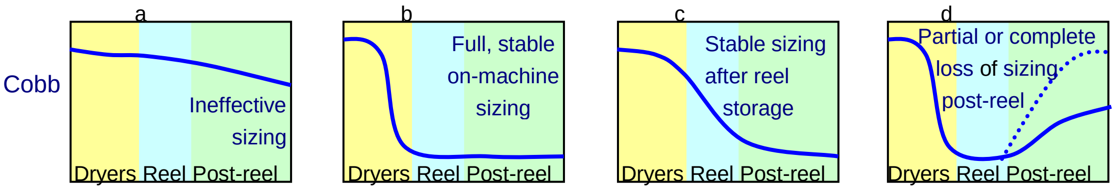
Effective paper sizing requires a very uniform coverage of the particulate surfaces and the distribution of the sizing chemical is thus critical to the expression of its functionality in the paper. The mobility of the sizing chemical within the drying section has a significant influence on its sizing efficiency as the ability to re-distribute itself is an effective way of overcoming any non-uniformity in size distribution during sheet formation. This means that the softening/melting point of the size is important. Finally, the conversion of the sizing agent from its non-sizing form to an active size is itself driven by the high temperatures experienced by the paper web in the final stages of drying.

There are three main sizing chemicals added at the wet end:

- ☐ rosin, which is the traditional wet end size used under acid conditions
- ☐ alkyl ketene dimer (AKD), which was the first synthetic size developed to function at neutral pH
- ☐ alkenyl succinic anhydride (ASA), which was developed slightly later than AKD as a neutral size.

Over the last 30 years, there has been a substantial swing away from traditional rosin sizing under acid conditions with alum to the use of AKD/ASA sizes under neutral/alkaline conditions. This started in the wood-free fine paper sector, where it was driven mainly by the desire to replace kaolin by calcium carbonate filler, the use of which is incompatible with acid conditions. This change in the chemistry of fine papers led to greater levels of calcium carbonate in recovered paper, so paper machines making recycled grades had to follow this trend by adopting a more neutral operation with either AKD, ASA or neutral rosin.

Papers are usually sized with any one of the above chemicals, but it is possible to use chemical combinations to bring together sizing benefits not possible with one chemical type. Liquid packaging products require rather special sizing, particularly if the product has to be aseptic. AKD size is able to give the required sizing level against acidic container contents, whereas rosin gives better resistance against the hydrogen peroxide used to sterilise the packaging. Combinations of AKD and ASA are also used for sizing liquid packaging boards and have also found useful applications in sizing wood-free papers filled with precipitated calcium carbonate.



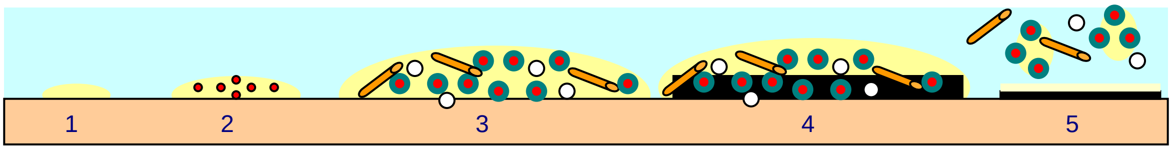
The picture at the start of this section gives typical sizing response curves for different furnish conditions assuming that the sizing develops fully on the machine, but this is not always the case, as shown in the further examples above (again all using the Cobb value as an index of sizing performance). The picture at left below (a) shows the case where sizing does not develop at all due to poor size quality, retention or curing. The second picture (b) shows the ideal situation where sizing develops fully during drying and remains at that level prior to use of the paper. All three wet end sizing agents can deliver this sizing pattern when working well. The next picture (c) shows a pattern typical of AKD sizing under certain conditions when the sizing is not fully developed at the reel, but continues during reel storage and is adequately sized by the time that the paper is used. The last picture (d) shows a pattern of complete on-machine sizing, but this is then partially or completely lost over time. This latter effect is known as size reversion or fugitive sizing and has been a particular problem with some AKD-sized papers, although it can also occur with rosin and ASA sized papers.

Slime

This is the common term for the mixed population of micro-organisms that form biofilms on the surface of submerged equipment, slime representing one of the most prevalent forms of deposition at the wet end of papermaking systems. There are many sources of both bacteria and fungi in the papermaking system and slime is perhaps the most obvious manifestation of their growth, but it is only one of several microbiological problems that accompany such growth.

It is possible to break down the life cycle of slime/biofilms into 5 stages, which is visualised below:

1. conditioning of the surface through the adsorption of organic and inorganic chemicals, which is very easy in papermaking due to the nature and quantity of substances present. This (and the next stage) can be minimised by maintaining adequate (self-cleaning) velocities, which is possible in pipes, but not usually within tanks.



2. attachment and colonisation by bacteria, which is helped if the adsorbed chemicals are available as a food source (eg starches) and by the production of extra-cellular polysaccharides (ECPs) by the bacteria. The latter have a broad chemical composition incorporating some monosaccharides present in hemi-celluloses (glucose, mannose and galactose) together with others such as fucose, rhamnose, glucosamine and galactosamine.
3. consolidation and maturing of the bio-matrix particularly by the ECPs with bacteria and fibres/fillers being captured from the bulk phase
4. as the film gets thicker, differentiation of the film into an anaerobic zone (probably black in colour due to the presence of ferrous sulphide) near the attached surface with this growth being more controlled by diffusion and changing to a more aerobic zone at the outer edge (if the passing liquid contains dissolved oxygen).
5. detachment (sloughing) of components into the bulk liquid to establish some sort of equilibrium with freshly-growing cells, this balance being very dependent on variations in nutrient availability and other environmental factors (pH, temperature, etc).

Any slime retained in the paper represents a weak area in the paper structure, which may lead to web breaks and the slime spot in the product detracts from its appearance and functionality. Slime can be controlled by the same hierarchy of techniques used for the control of general microbiological problems, but some of these, notably the dosing of dispersing chemicals to prevent microbial aggregation or of chemicals to inhibit biofilm formation, are specific to slime prevention. However, slime is still most commonly controlled by dosing of biocides to the papermaking stock/waters.

An important element in the control of microbial growth is monitoring the effectiveness of the control system being used. There are a number of techniques that offer greater rapidity and ease of use than the traditional colony counting method for estimating the total number of microbes in a sample (see further here). However, this does not provide specific information on the potential for slime growth as not all suspended (planktonic) bacteria can become attached. The levels of slime can be monitored by simple observation at key locations where slime is known to accumulate or by insertion of slime coupons for periodic inspection. As the slime tends to develop anaerobic zones (phase 4 in above classification) close to the surface, the level of anaerobic activity can be monitored via the build-up of anaerobic degradation products (eg volatile fatty acids and sulphides) in the bulk water system.

Over recent years, a number of automatic slime measurement systems have been in the process of development, initially for laboratory simulation systems, but with the possibility of on-line application. There are two different approaches:

- slime depth monitoring with a metal/plastic sensor, that is continuously or periodically exposed to an irradiation source with the degree of attenuation being related to the slime accumulation. This approach is being pursued by at least two biocide suppliers.
- slime depth monitoring with a quartz crystal microbalance (QCM) from the Swedish company, Q-Sense AB. The microbalance consists of a thin quartz disc sandwiched between a pair of electrodes. The quartz crystal can be made to oscillate by applying an AC voltage between its electrodes. When a thin film is attached to the sensor crystal, the frequency decreases and, if the film is thin and rigid, the decrease in frequency is proportional to the mass of the film. Laboratory testing has shown that this system is very sensitive to the early stages of biofilm attachment, when visual assessment is often inconclusive.

Slip

This term is used to describe papers with a low friction coefficient.

SMA

This is an abbreviation for styrene-maleic anhydride sizes.

Smoothness

This surface paper property is very important for some grades of paper (eg printing papers). It is measured by air leak testers (also used for porosity measurement), where the air application head is lightly pressed against the paper surface and the other side covered with an impermeable backing. Air can only leave the air application head by virtue of the surface imperfections that give rise to surface roughness. The airflow leaking out of the head is thus an index of roughness/smoothness, the higher the value the less smooth the surface. There are various commercial instruments using this principle, the Gurley and Bekk testers giving the time taken for a fixed air volume to pass and the Bendtsen and Sheffield testers giving the air flow rate. The Parker Print-Surf also uses the air leak principle, but in this case to measure the gap between the paper and contacting surfaces. Smoothness is important in relation to paper printability, which requires good contact between the paper and the printing cylinder. As improved contact can be achieved by increasing the pressure between the paper and opposing surfaces, the compressibility of the paper also influences printability and this parameter can also be quantified with the Parker Print-Surf.

Soap

This is the term for the substance formed when a long-chain fatty acid is saponified with an alkali such as sodium hydroxide. Soaps may be present in papermaking from two main sources:

- Kraft pulps due to their formation from fatty acids present in the wood's extractives fraction
- deinked pulps, due to the use of soaps to maximise ink removal in the flotation stage.

In both cases, the soap levels reaching the paper machine are dependent on the efficiency of pulp washing and on the level of calcium ions, as these will precipitate the calcium soap and increase the soap's carry-over with the pulp.

Soda

This is an older term for sodium hydroxide as in soda pulping.

Soda ash

This is a colloquial term for sodium carbonate.

Soda pulp

These pulps are little produced today except in the non-wood pulp sector, but soda pulping was the first type of chemical pulping process. As an alkaline pulping process, it is the fore-runner of the Kraft process, which is the dominant chemical pulping process today. The soda process uses sodium hydroxide as the sole cooking chemical, but it can be used in more modern variants such as soda-AQ.

Sodium

Sodium (Na, atomic mass 23) is the second element in Group I (the alkali metals) of the Periodic Table. The sodium ion (Na^+) is quite common in fresh waters and features in many compounds (sodium salts) used in papermaking.

Sodium aluminate

This is an alkaline aluminium compound with the formula, $NaAlO_2$. It is considerably more expensive than alum and is not commonly used in papermaking today.

Sodium bicarbonate

This electrolyte ($NaHCO_3$) is sometimes added as a source of bicarbonate alkalinity with AKD sizes to boost their sizing efficiency (see this example).

Sodium bromide

This simple salt (NaBr) is used to generate sodium hypobromite and hence hypobromous acid through its reaction with sodium hypochlorite:

$$NaBr + NaOCl \rightarrow NaCl + NaOBr$$

Sodium carbonate

This basic chemical (Na_2CO_3) is commonly referred to as soda ash. It is not used extensively in papermaking, the most common application possibly being its use as a source of alkalinity with AKD sizes to boost their sizing efficiency. As the pK value for the carbonate/bicarbonate equilibrium is about 10 at 25°C, any added carbonate will be present as bicarbonate at neutral pH levels. Soda ash is thus a stronger alternative to adding bicarbonate directly in this form.

Sodium chloride

This well-known simple electrolyte (NaCl) is present in most fresh waters, but only at a low level (usually < 100 mg/l unless it is a ground water subject to saline intrusion) and is the dominant dissolved substance in sea water. It is sometimes used in papermaking as a size press additive to increase the surface conductivity of the paper for certain printing applications (eg laser printing) and it is often present as a residue in pulps that have been bleached with chlorine-containing chemicals. Although it is usually not the dominant electrolyte in machine waters, it has often been used in model studies to evaluate the effect of dissolved electrolytes on various aspects of wet end chemistry (eg its effects on the adsorption of anionic starch, cationic starches, polyacrylamide and PAE resin).

Sodium dithionite

This is an alternative name for sodium hydrosulphite.

Sodium hydrosulphite

This chemical ($Na_2S_2O_4$) is also known as sodium dithionite and is used for bleaching of mechanical pulps and bleaching/colour stripping of deinked pulps and mill broke. It is a reductive bleach with the following half-cell reaction:

$$S_2O_4^{2-} + 4OH^- \rightarrow 2SO_3^{2-} + 2H_2O + 2e^- \text{ where } E_H^o \text{ (redox potential)} = +1.1 \text{ volts at } 25^oC$$

Its reducing power is strongest under alkaline conditions, but hydrosulphite bleaching is usually carried out under slightly acidic conditions (pH 5-6) where the half-cell potential is about +0.9. Sodium hydrosulphite can be supplied in a powder or solution form for direct dosing, but the powder is subject to spontaneous combustion in the presence of air and must be kept in closed containers. Hydrosulphite can also be generated in situ by the reaction between sodium bisulphite and sodium borohydride.

In aqueous systems, its reaction with pulp suffers from two competing reactions:

- decomposition to give a mixture of bisulphite and thiosulphate ions:

  $$2S_2O_4^{2-} + H_20 \rightarrow S_2O_3^{2-} + 2HSO_3^{2-}$$

- oxidation by any oxygen dissolved or entrained in the pulp suspension to give a mixture of bisulphite and bisulphate ions:

  $$2S_2O_4^{2-} + H_20 + 0_2 \rightarrow HSO_4^{2-} + HSO_3^{2-}$$

Air must thus be excluded from the bleaching system. Typical bleaching conditions are doses of up to 2% on pulp for 1-2 hours at about 60^{o}C and a consistency of 5-10%. As heavy metal ions adversely affect bleaching efficiency, it is common practise to add chelants or sodium silicate to the bleaching suspension. It has the advantage over its chief competitor (hydrogen peroxide) that there is very little dissolution (loss of yield) when bleaching is conducted under acid conditions.

Sodium hydroxide

This chemical (NaOH), also commonly referred to as caustic soda, is widely used in many industries for pH control. It is manufactured from sodium chloride by various electrochemical methods, the co-product being chlorine and is widely available in solutions of various strength. In papermaking, its main use is for pH control at the wet end and as part of "system-cleaning" formulations.

Sodium hypobromite

This salt is not used as such in papermaking, but is generated from the reaction of sodium bromide with sodium hypochlorite. As with chlorine compounds in aqueous systems, the actual bromine species depends on pH through its hydrolysis with water:

$$Br^- + OBr^- + 2H^+ \leftrightarrow HOBr + HBr \leftrightarrow Br_2 + H_2O$$

The pK value for ionisation of hypobromous acid bromine with water (8.5 at 20^{o}C) is higher than that for chlorine, so there is a much higher proportion of the most biocidally active species, HOBr, at pH values above 7 (see this figure). Bromine compounds also have a lesser tendency to react with organic compounds to form halogenated organics. An alternative source of hypobromous acid is the brominated hydantoins.

Sodium hypochlorite

This very common chemical is manufactured from chlorine gas and caustic soda by the simple reaction:

$$NaOH + Cl_2 \rightarrow NaOCl + NaCl$$

Sodium hypochlorite is a reasonably strong oxidising agent, but not as strong as chlorine:

$$OCl^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^- \text{ where } E_H^o \text{ (redox potential)} = +0.9 \text{ volts at } 25^oC$$

Along with chlorine, it used to be used extensively in the bleaching of chemical pulps, but, in this case, in the later bleaching stages. It does not have the same tendency to generate chlorinated organics, but it use was strongly implicated in the generation of chloroform. Although the use levels were never as high as that of chlorine, its use has also declined because of this latter problem.

Sodium hypochlorite is used for fresh water disinfection at paper mills, but its uses for bleaching of deinked pulp/coloured broke and dispersion of wet strengthened broke have been under pressure for similar reasons to those in the bleaching of virgin pulp. In its role as a biocide, the aqueous chemistry of sodium hypochlorite is important:

$$Cl^- + OCl^- + 2H^+ \leftarrow\rightarrow HOCl + HCl \leftarrow\rightarrow Cl_2 + H_2O$$

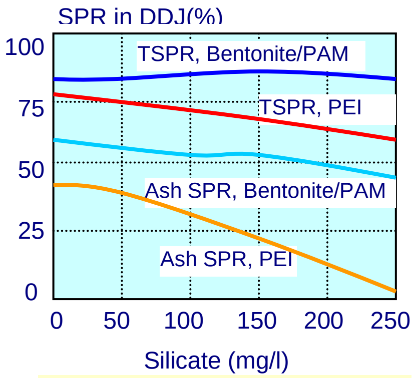
The pK value (about 7.5 at 20°C) for the ionisation of hypochlorous acid (HOCl) means that, as the pH get closer to 8, most of the oxidising power is present as the less biocidally-active hypochlorite ion. This is the main reason why sodium hypobromite has become popular for disinfection of waters above pH 7. An alternative source of hypochlorite/hypochlorous acid is the halogenated hydantoins.

Sodium silicate

These soluble salts are sometimes referred to as water-glass and are produced by reacting silica (SiO_2) in the form of sand with an alkali such as sodium hydroxide or carbonate. The chemistry of the products thus formed is complex depending on the ratio of silica to alkali. The simplest compounds are sodium metasilicate (Na_2SiO_3) and sodium orthosilicate (Na_4SiO_4), but silicate complexes can also be formed in linear and cyclic forms with the silicon atoms connected by oxygen bridges. All the sodium silicates produce strongly alkaline solutions as they are the salts of a weak acid and strong base. Sodium silicates are also the starting point for the production of colloidal silica.

Sodium silicates are not used in papermaking, but they are used as stabilisers in bleaching with hydrogen peroxide, sodium hydrosulphite and FAS. In deinking, they are also used as a source of alkalinity and for their ability to stabilise suspended particles due to adsorption of silicate. Residual silicates in deinked pulps and in bleached mechanical pulps can contribute to anionic trash levels on the paper machine, but, as with other dissolved substances, this depends on the efficiency of washing/thickening of the bleached pulp. In one case reported for a laboratory study, the cationic demand increased by about 1 eq/tonne pulp for each 1% dose of silicate on pulp.

An illustration of the adverse effect of residual silicate from deinking on single pass retention (SPR) is shown at right for a newsprint furnish containing 40% deinked pulp. It is clear that silicate adversely affects retention for both the polyethyleneimine (PEI) and bentonite/anionic polyacrylamide, but it is most evident for the SPRs of the filler component. Although the bentonite-based system is better able to withstand the silicate ions, there is still a significant drop in ash SPR. This study also showed a similar difference in performance between a bentonite-based system and a dual polymer (polyamine/polyacrylamide) system in the presence of silicate (up to 1000 mg/l) for the clarification of the deinking wastewater.



Reference: Tremont in Pulp Paper Canada, 1995, 96, 12, 101-104.

Sodium sulphate

This simple electrolyte (Na_2SO_4) is not used directly in papermaking, but it is added in the Kraft pulping process although its active form is as sodium sulphide. It is commonly known as salt cake.

Sodium sulphite

In papermaking, this reducing agent (Na_2SO_3) is occasionally used to neutralise any residues of chlorine bleaches, which may otherwise cause problems, eg when some wet strength agents are used. Sodium sulphite is also used in the production of some pulps, notably NSSC pulps and some chemithermomechanical pulps.

Softener

This is a class of chemicals used mainly in the tissue sector to enhance the softness of the product. They are usually based on quaternary ammonium compounds such as $R_2(CH_3)_2N^+ Cl^-$, where R is a long-chain fatty acid such as palmitic and/or stearic acids or a fatty acid ester. They can be added either at the wet end or sprayed onto the paper web or the drying cylinder. Chemicals used as debonding agents and absorbency aids are rather similar.

Softness

Softness is a rather subjective and complex property of paper, which depends on the interaction between a number of paper characteristics such as fibre flexibility, strength and bulk. There are two types of softness:

- ❑ surface softness, which is the softness perceived by the fingertips as they softly touch the paper
- ❑ bulk softness, which is the softness perceived when the paper is crumpled in the hand.

The softness of paper is influenced by the types of pulp used, the type of forming process, the extent of sheet pressing and creping in addition to the application of chemical softeners. The term "softness" may also be used in the context of the properties of fillers and pigments and in relation to the absence of hardness in water.

Softwood

This is the wood from coniferous trees, which is widely used for conversion into papermaking pulps. The name reflects the fact that the wood in these trees is somewhat less dense than in hardwoods, typically around 400 kg dry substance per m^3 of total wood or around 500 kg dry substance per m^3 of the fibre wall. Softwoods are older in evolutionary terms than hardwoods and thus have a much simpler cell structure. This is dominated by tracheids, which are long tapering cells that run longitudinally along the trunk and have a pitted surface. Despite tracheid being their correct name, in practice they are commonly referred to as fibres. Softwood tracheids can be up to 4 mm in length with a fibre diameter of 30-40 microns. Softwoods contain no vessel elements (only present in hardwoods), but do have some parenchyma cells present. A summary of some physical properties of softwoods is shown in the table below. The distribution of fibre lengths for a softwood pulp is shown here.

Softwood	Fibre length (mm)	Fibre diameter (µm)	Fibre wall thickness (µm)	Coarseness (mg/m)
Spruce	3.3-3.5	25-30	2.2.-2.3	0.15-0.3
Southern Pine (USA)	4.6	35-45	2-5	0.2-0.3
Pine	3-4	25-45	3-4	0.2-0.5

The cellulose content of softwoods is similar to that of hardwoods (43-45%). Softwoods have a higher lignin content than hardwoods (typically 26-32% compared to 20-25%) and lower hemi-cellulose content (typically 25-30% compared to 30-35%). The extractives content of softwoods (typically 2-5%) is higher than hardwoods and may (notably for pines) exceed 10%. The main types of softwood grown for papermaking are spruce, pine and fir with different species being used depending on the growing region. Softwoods are used to make mechanical, unbleached Kraft and bleached Kraft pulps and are widely used for their high strength attributes in nearly all grades of paper.

Solubility

The solubility of materials in water is essential for many papermaking substances as this allows the material to be uniformly applied to the paper substrate, particularly during surface application. This also applies to water-soluble chemicals added at the wet end, but they have to be efficiently adsorbed on the particulate matrix to be retained in the paper. Apart from dissolved solids in the fresh water, other dissolved substances at the wet end originate by incidental dissolution from particulate materials such as pulps and this is generally undesirable.

The solubility of a substance in water is determined by the free energy change associated with the substance becoming a dissolved entity. In order for a substance to dissolve and form a true solution, the interaction of the solvent with the substance (hydration in the case of water) has to overcome the cohesive forces between individual molecules or ions. The behaviour of substances (solutes) placed in water thus depends on the net outcome of solvent-solvent, solvent-solute and solute-solute interactions, the result (solubility or insolubility) being whatever lowers the system's free energy.

The interaction of water with the solute leading to partial or complete dissolution may be through any of the following mechanisms:

- an ion-dipole interaction, eg between water and anions such as sulphate or cations such as sodium
- the formation of co-ordinate bonds, eg between water and aluminium ions
- hydrogen bonding between water and substances containing -OH or -NH- groups.

Water has a high dipole moment due to its asymmetric structure and this gives it a very high dielectric constant, which makes it a very good solvent for other polar substances such as electrolytes. The solubility of electrolytes is defined by the solubility product (K_{sp}):

$$MX \rightarrow M^{+} + X^{-}$$

$$K_{sp} = a_M . a_X = (\gamma_M . c_M)(\gamma_X . c_X)$$

where a, γ and c are the ion activities, activity coefficients and concentrations

In dilute solutions of an indifferent electrolyte (ie one not containing the ions M^+ or X^-), the solubility of MX has to increase in order to maintain the value of K_{sp} as both γ_M and γ_X become smaller fractions. This is sometimes referred to as "salting in", whilst "salting out" is a term applied to the use of much higher concentrations of salts to reduce the solubility of another substance. This effect has nothing to do with activity, but is probably related to the competition for water between the dissolved material and the added salt, with the latter winning when sufficient is added. Another well-known solubility phenomena is the so-called "common ion" effect, where the addition or presence of a common ion (say M^+ in the above example) reduces the solubility of the other (in this case X^-) in order to maintain the value of K_{sp}.

The solubility of gases is determined by Henry's Law. The solubility of two gases in particular is important in papermaking - oxygen and carbon dioxide. Other gases that can be present in the papermaking system (and cause problems) are hydrogen sulphide and hydrogen, both derived from microbial activity under anaerobic conditions.

The extent of dissolution of organic substances from pulps is not usually constrained by the solubility factors described above for inorganic electrolytes and gases. Most of the organic substances are hydrophilic polymers (eg hemi-celluloses, starches, etc) with many hydroxyl groups that can hydrogen bond with water. The most important facet that limits the dissolution of such polymers is their ability to diffuse through the fibre's pore structure which depends on the extent of fibre swelling, which is in turn affected by pH, electrolyte content and temperature. Pulp swelling is not likely to limit the dissolution of electrolytes (being very small ions) from the pulp so the resulting electrolyte concentration will exert a feedback effect on fibre swelling, which will then influence the dissolution of organics.

Solute

This is the chemist's term for the material that dissolves in a solvent to form a solution.

Solute exclusion

In papermaking, this principle is made use of to quantify pulp swelling, but it is also pertinent to the behaviour of water-soluble polymers at the wet end. As an analytical technique, solute exclusion (also known as gel permeation chromatography) uses a matrix of known pore size to characterise the molecular size and hence mass of polymers. A version of this technique (inverse solute exclusion) is used to measure the fibre saturation point of pulps. In wet end chemistry, the adsorption of added polymers may be limited by their inability to gain access to some of the internal surfaces of fibres due to their molecular size being too large to penetrate the fibre's pore structure. This phenomenon is also relevant to charge titrations involving polymers. In the opposite sense, a similar size restriction may also limit the dissolution of polymers (eg hemi-celluloses) from pulps at the wet end.

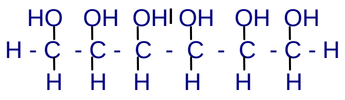
Solution

This is defined as a homogeneous mixture of chemical species (the solute) that are dispersed on a molecular scale in a solvent.

Solvent

This is the chemist's term for the liquid that dissolves a solute to form a solution.

Sorbitol



$$\mathrm{H-\underset{H}{\overset{HO}{C}}-\underset{H}{\overset{OH}{C}}-\underset{H}{\overset{OH}{C}}-\underset{H}{\overset{OH}{C}}-\underset{H}{\overset{OH}{C}}-\underset{H}{\overset{OH}{C}}-H}$$

This chemical is used as a humectant in papers where greater moisture retention is needed. It is a hexahydric alcohol (formula shown at right), which is made by reduction of glucose. Its humectant properties arise simply as a result of the large number of hydroxyl groups for hydrogen bonding with water molecules. It is always added by some form of surface application.

Sorption

This term is used to cover the combined processes of absorption and adsorption.

Specific heat

This is defined as the amount of energy required to increase the temperature of unit mass of substance by 1^{o}C. Water has a very high specific heat (4.18 J/g.^{o}C at 20^{o}C), which is due to its low thermal conductivity (0.58 W/m.^{o}C) , which is in turn due to its strong inter-molecular attractive forces. The specific heat of cellulose is much lower at about 1.3 J/g.^{o}C (thermal conductivity = 0.13 W/m.^{o}C).

SPR

This is an abbreviation for single pass retention.

Spraying

This is a technique for the surface application of certain chemicals to the paper web. The main application is the spraying of a suspension of uncooked starch either for improvement of surface strength or, on multi-ply products, for the improvement of ply bond. This technique has also now been developed for normal pigment coating to the dried paper web, but this is at an early stage of full-scale application.

Spreading

The term refers to the ability of liquids to extend across the surface of another liquid or a solid by wetting it. This can be quantified through a spreading coefficient (S) when a system is at equilibrium. For water on a solid surface (see picture under interfacial energy), the equation is as follows:

$$S = \gamma_{SA} - \gamma_{AW} - \gamma_{SW}$$

where γ_{AW} = interfacial tension between air and water
γ_{SA} = interfacial tension between the solid and air
γ_{SW} = interfacial tension between the solid and water

Using the Young equation, the above equation for S reduces to:

$$S = \gamma_{AW}.(\cos\theta - 1) \text{ where } \theta = \text{contact angle}$$

The spreading coefficient is a measure of the difference in surface energy between the dry solid and the moist solid covered by a macroscopic film of liquid. When $S < 0$ (positive contact angle), a surface can be partially wetted, but when $S \geq 0$ (zero contact angle), a surface can be fully wetted.

Spruce

This is a type of softwood tree, which is widely used to make mechanical and chemical pulps for papermaking. Spruce has a moderate extractives content, which has been quoted for *Picea abies* as 1-2% of the dry wood, being composed of about 60% neutral substances (mainly fatty acid esters), about 10% free fatty acids and about 25% resin acids. Spruce wood contains about 15 μeq/g of carboxyl groups from fatty or resin acids in extractives and about 70 μeq/g from glucuronoxylan against a total carboxyl content of 150-250 μeq/g. However, the accessible charge is only some 70 μeq/g, although this doubles in value after hydrolysis of carboxyl esters. In the thermo-mechanical pulping of Norwegian spruce, around 40 kg wood substances/tonne pulp can be dissolved, the largest fraction being the galactoglucomannans. Data on the distribution of anionic substances in unbleached spruce TMP is given here and on the changes that take place on peroxide bleaching of spruce stone groundwood here.

Squareness

This term refers to the ratio of a paper's tensile strength in the machine direction (MD) to that in the cross direction (CD). For a laboratory handsheet, this value is usually unity as the fibres are arranged randomly. As fibres on a paper machine tend to be aligned in the machine direction, the MD tensile strength is always greater than the CD tensile strength and the squareness is thus always greater than one. Fibre alignment is influenced by factors such as the efflux ratio.

SR

This is an abbreviation for Schopper-Riegler.

SRB

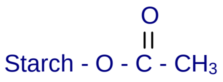
This is an abbreviation for sulphate-reducing bacteria.

Starch, coating

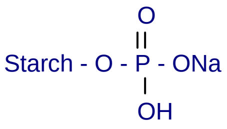
The use of starches in coating represents a relatively small proportion (about 10%) of total starch use in papermaking. In coating, starch functions primarily as a pigment binder, but it also influences the rheology of the coating mix and its water retention. As is evident from this table, starch is not the strongest binder per unit mass amongst the common binder chemicals, but it is very cost effective due to it being much lower in price than the alternatives. Starch thus tends to be used in greater quantities (both as a proportion of the pigment and as a proportion of the binder component) as the solids content of the coating mix is reduced as this requires higher binder levels. Because of its cost-effectiveness, it is the most common co-binder for use with latices to give the required rheological characteristics in the coating mix.

Starch esters

These starches are produced by reacting a starch suspension with a suitable esterifying agent such as acetic anhydride to form acetylated starches (as shown near right) or with inorganic phosphates to form starch phosphates (far right). The main acetylation reaction is with the hydroxyl group on carbon 2 and then with the CH_2OH group, but very little with the hydroxyl group on carbon 3 (see glucose for numbering pattern). By contrast, the phosphate ester is largely at carbon 6 on the pendant $-CH_2OH$ group. The maximum degree of substitution is only about 0.2, but this is adequate to prevent hydrogen bonding between adjacent molecules and thus improve its solution stability. The nonionic acetylated starches are widely used for surface application and the anionic starch phosphates can be used for wet end application under certain conditions (see anionic starches).



$$\text{Starch} - O - \overset{\overset{\displaystyle O}{\|}}{C} - CH_3$$

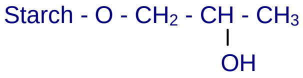


$$\text{Starch} - O - \underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle O}{\|}}{P}} - ONa$$

Starch ethers

These starches are produced by reacting an alkaline starch suspension with either ethylene or propylene oxides to form the hydroxyethyl starch ether (see right above) or hydroxypropyl starch ether (right below). Like the acetylated starch esters, the reaction is mainly at the hydroxyl on carbon 2 with a degree of substitution up to 0.1. Etherification lowers the starch's gel point such that a hydroxyethyl starch swells in cold water when the DS is about 0.3. All starch ethers have a much reduced retrogradation tendency compared to native starches and contribute a high water retention and binding power to coating mixes. In addition, they are better film-formers than native or oxidised starches and so are widely used for surface application.

$\text{Starch} - O - CH_2 - CH_2 - OH$



$$\text{Starch} - O - CH_2 - \underset{\underset{\displaystyle OH}{|}}{CH} - CH_3$$

Being nonionic, they find no significant application at the wet end, unless the etherifying agent contains a charged group. Anionic starch ethers are formed by reacting starch with chloroacetic acid to form carboxymethyl starches, which are structurally similar to carboxymethylcellulose. Of much greater importance are the cationic starches, which are starch ethers with a cationic group within the substituting entity.

Starch, general

Starches represent the third largest class of raw materials used in papermaking and are the major type of additive used to enhance the dry strength of paper. Their precise mode of action depends on where they are added and this can be at any of four positions:

- ❑ as a wet end additive in solution form to improve the bonding between particulate surfaces. This application always uses a modified starch in order to ensure effective adsorption on the particulate matrix. Starches may also be present at the wet end from their use as emulsifiers for sizing chemicals such as AKD and ASA. Although not added directly as a strength additive, the starch emulsifier can contribute to sheet strength once it is incorporated in the sheet and released from its emulsifying role.
- ❑ by spraying an uncooked starch suspension onto the surface of the paper, most commonly between the plys on multi-ply products in order to improve the ply bonding. This application usually uses an unmodified starch.
- ❑ by impregnation of the paper surface with a starch solution in order to improve the paper's surface strength. This is most commonly done by immersion of the web at a size press, where other chemicals may also be added. This application makes use of the ability of many starch types to form a thin, coherent film, but the overall distribution of the starch between the surface film and penetration into the body of the paper is controlled by a number of parameters, notably the starch's viscosity.
- ❑ by incorporating a starch solution into a coating formulation, where the starch's function is as a binder for the mineral pigment. Starch is rarely used as the sole binder and is usually a co-binder with synthetic latices such as styrene-butadiene polymers. An exception to the use of starch solutions in coating is the use of starch granules in coating carbonless-copy papers.

Starch is also used in the converting of some paper products, notably of corrugated cases.

Starch is a natural, renewable and biodegradable material obtained from a variety of sources that can be broken down into two classes:

- ❑ the cereal starches such as wheat and maize/corn starches
- ❑ those where the starch is stored in the root/tuber such as potato and tapioca starches.

Each type of starch has a characteristic granule shape and size distribution with potato starch granules being the largest (see table below). Starches contain two different carbohydrate polymers - amylose and amylopectin plus some fatty materials. The amylose/amylopectin balance of most starches varies in the range 20-30/70-80%, but the so-called waxy starches (notably maize) contain no amylose at all. The amylopectin fraction makes the more significant contribution to starch’s strengthening effect because of its greater mass contribution and its much higher molecular mass compared to amylose.

Characteristics of main starch sources

Starch property	Potato	Corn/maize	Wheat	Tapioca
Granule size (µm) and shape	5-100 oval	2-30 round	1-45 oval	4-35 oval
Amylose content (%)	20-23	25-28	26-27	17-20
Amylopectin content (%)	77-80	72-75	73-74	80-83
Molecular weight amylose	0.5-1	0.1-0.2	0.1-0.2	0.5-1
(M Daltons) amylopectin	200-500	200-500	200-500	200-500
Fat content (%)	0.1	0.8	0.9	0.1
Starch-bound phosphate (%P)	0.08	0	0	0
Moisture content (%)	18-19	12-13	12-13	12-13
Gel temperature (°C)	60-65	65-80	70-85	60-65

The other two important substances present in starches are fatty material and phosphorous. Only the cereal starches have a significant fat (lipid) content, which is partly responsible for their higher gel temperature and for the slight opalescence of cereal starch solutions. The fatty material is held as an inclusion complex with the amylose fraction. Some of the phosphorous is associated with the fatty material, but only potato starches have phosphate groups in place of some hydroxyls on the pendant -CH_2OH group within the amylopectin fraction. This gives potato starches some anionic character and helps potato starch swell at lower temperatures than other starch types.

The molecules within the starch granule are built up during biosynthesis in concentric layers, but with a radial orientation of the amylose and amylopectin molecules. As with the chemically-similar cellulose, the starch molecules are associated in either ordered crystalline micelles or random, amorphous regions, but it is the amylopectin fraction that plays the major role in the granule's structural integrity and insolubility in cold water. Hydrogen bonds hold the molecules together in the crystalline regions, but, as the water temperature rises, the granules in the amorphous areas begin to swell thus disrupting the overall cohesiveness of the granule. At a certain temperature reflecting the molecular association within that particular starch, the viscosity of the solution begins to rise rapidly. This is the gel or pasting temperature, which varies between the starch types (see above table). With further heating, the solution viscosity increases to a maximum and then declines as the water penetrates the crystalline regions and disrupts the inter-molecular hydrogen bonding. Once dissolved, stored starch solutions have a tendency to become cloudy over time, a phenomenon known as retrogradation or set-back.

Starches are nearly always used in a solution form in papermaking, the exceptions being:

- ❑ pre-gelatinised starches, which have already been cooked by the supplier and re-dried
- ❑ starches used in a suspension form for surface application by spraying
- ❑ starches used as spacers in the capsule coatings of carbonless-copy papers.

Most starches thus have to be cooked on-site either in batches or by continuous cooking, the latter being the most common technique. This may be a purely mechanical process as used for starches modified by the starch manufacturer or the so-called conversion processes in which native starches are cooked in a thermo-chemical process or an enzymatic process. These latter types are the most widely-used starches and are added at the size press, but very rarely at the wet end as they have little affinity for the particulate matrix and are thus poorly retained.

Uncooked or partially-cooked native starches have sometimes been used at the wet end as they could be retained by the normal filtration mechanisms applicable to other fine particulate solids such as fillers, but this is not a commonly-used option. Nearly all wet end starches are modified chemically to enhance their affinity for the particulate matrix, normally by making the starch cationic (amphoteric in the case of potato starches) or, less commonly, by making the starch anionic (more anionic in the case of potato starches). The range of chemical modifications possible is summarised in the table below.

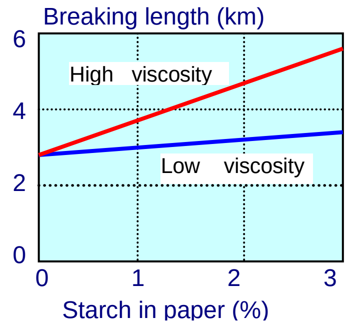
Summary of main starch types

Starch type	Treatment	Characteristics
Pre-gelatinised	Cooking and drying	Cold water solubility
Thermo-chemical converted	On-site with persulphate or peroxide in batch or jet cooker	Lower viscosity
Enzyme-converted starch	On-site with amylase after cooking	Lower viscosity
Thermally-modified	Acid treatment of hot suspension	Lower viscosity and retrogradation in nonionic form
Oxidised	Hypochlorite on suspension	Lower viscosity and retrogradation; better viscosity stability
Esterified	Acetylation of alkaline suspension	Easy cooking; low retrogradation; good film-forming
Etherified	Ethylene/propylene oxide on alkaline suspension	Good viscosity stability; lower retrogradation; good film-forming
Cationic	Etherification, but with quaternary-nitrogen substitution	Excellent wet end adsorption; good retention on recycling broke
Anionic	Esterification with phosphate or etherification with anionic substitution	Good wet end adsorption in presence of cationic substances
Cross-linked	Reaction with bi-functional chemicals such as borax and epichlorhydrin	Lower swelling and gelatinisation; less hydrophilic character

There have been a lot of studies on the use of starches in papermaking, which, unlike those for many other papermaking chemicals, have been based on the direct analysis of starch in terms of its adsorption on fibre and/or retention in the paper. This is possible because there are a number of relatively simple analytical techniques for its analysis, three of the common methods being:

- total carbohydrate analysis by the phenol-sulphuric acid procedure which generates an orange coloration for measurement. This technique is best applied to dissolved starches, but suffers from the fact that it also measures any other carbohydrate such as dissolved pulp hemi-celluloses.
- "starch" analysis by the well-known coloration with iodine, but this technique is more sensitive to the amylose fraction of starch and the colour intensity depends on the starch's molecular weight.
- enzymatic (or acid) hydrolysis to glucose followed by glucose analysis by any of several techniques, eg measurement of hydrogen peroxide generated by glucose oxidase enzyme. This technique may also be applied to papers by treating a sample with amylase enzymes to solubilise the starch prior to final analysis as above.

As summarised above, starch in all its guises is used mainly for its adhesive and, with suitable substrates like fibre, its cohesive characteristics, which can add strength to all paper products. There is one important quality of the starch behind this strengthening ability and this is the long chain length of starch, notably of its amylopectin fraction. The example at right illustrates the very different strengthening ability of two starches, which have been cooked to different viscosity levels. This emphasises two important points about starch use - the importance of not over-cooking a starch and the need for controlling the microbial breakdown of cooked starches.



Source: Budd in Pira Report PB4R, 1986.

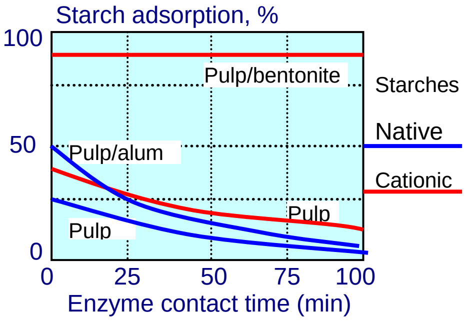
Starch, wet end

Wet end addition of starch represents a moderate, but growing, proportion of starch use in papermaking. At present, this amounts to about 20% of total starch use by weight, but a higher proportion (around 30%) in monetary terms as all wet end starches are modified by the manufacturer to maximise their retention. Because these starches are added to the stock suspension prior to sheet formation, they are more uniformly distributed within the paper matrix than when added to the paper surface and thus improve the overall bonding within the sheet. For this reason, wet end starches are used in many paper grades:

- ☐ in most printing/writing grades in order to compensate for the loss of strength resulting from the presence of filler
- ☐ in some packaging grades, notably those made from recycled pulps, in order to compensate for the weaker strength of recycled fibres
- ☐ in tissue and towel grades in order to compensate for the common absence of any pulp refining.

The key requirement for wet end starches is that they must be efficiently adsorbed on the particulate matrix in order to be retained effectively. As the particulate matrix in papermaking is normally negatively-charged, this type of starch is normally (but not always) a cationic derivative. As a cationic polymer, it can also assist in the aggregation of fine particles and this ability is utilised in a number of retention/drainage aid systems. In systems which already contain other cationic chemicals or where the water contains high electrolyte levels or anionic trash, anionic starches may be more effective. Starches that possess both anionic and cationic character (amphoteric starches) are also used at the wet end.

One of the important Issues in the use of any starch at the wet end is its susceptibility to microbiological breakdown. Without adequate control, this causes not only a range of microbiological problems, but it can also reduce the starch's essential ability to adsorb on the particulate matrix and its overall functionality. This is illustrated at right for different systems containing 3% added starch on pulp, which were deliberately treated with an amylase enzyme to break the starches down. The almost complete loss of adsorption by the unmodified starch is not unexpected, but it is interesting to see that the cationic starch residues were still cationic enough to be well adsorbed by the pulp/bentonite system.



Source: Webb in Pira Report PB2R, 1982.

One of the other driving forces for the development of new wet end starches has been the desire to eliminate the addition of starch at the size press and thus increase production through not having to dry the paper twice. A limiting factor in achieving this with cationic starch alone has been the difficulty in retaining enough starch cost-effectively and the possible adverse effect of high starch doses on drainage (see this example). The efficiency of wet end starch addition at high doses can be improved by several techniques, but there are two basic approaches:

- ❑ addition of uncooked or partially-cooked starch granules or starch re-precipitated from solution, in which the starch could be retained by the normal hetero-aggregation mechanism with the rest of the particulate matrix using conventional retention aids.
- ❑ addition of two materials with opposite charges such as an anionic starch with a cationic polymer; an amphoteric or cationic starch with an anionic, amphoteric or cationic polyacrylamide; or a cationic starch with an anionic wet-end starch. In all these cases, the two materials may be mixed before starch cooking or cooked separately and then combined prior to addition or dosed separately.

Starch, size press

Addition at the size press represents the largest application (about 70% of the total) for starches in papermaking. The main reason for adding starch at the size press (rather than at the wet end) is to concentrate the starch at the paper surface and improve the surface strength through starch's excellent film-forming ability. The improved surface strength gives greater pick/linting resistance (of most importance for printing papers) and stiffness (of most importance for packaging grades). Another factor relates to the quantity of starch that is required to deliver the desired improvement in strength. When this starch dose is high (say, above around 20 kg/tonne), it can be difficult to retain this quantity cost-effectively at the wet end and, as wet end addition would also involve the use of a modified starch, the total costs (even with high starch retention) could be unacceptably high.

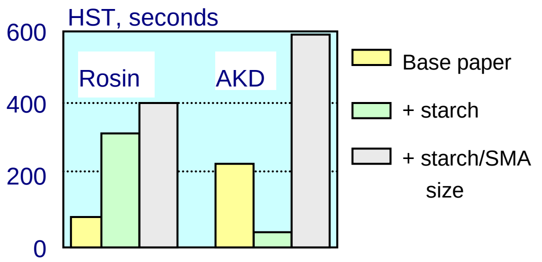
Although surface application has the potential to keep the starch largely at the paper surface, the degree of penetration into the base paper (the z-direction distribution) can be controlled through starch selection and control of the solution viscosity. Base paper characteristics are also important, notably its degree of sizing and moisture content. Overall starch pick-up is determined by a combination of the solids content of the starch solution and its viscosity. For film presses, starch pick-up also depends on the applied film thickness, which in turn depends on the paper's ability to absorb the solution rapidly without allowing a small pond (which would cause splashing) to build-up.

The main starches added at the size press are:

- ❑ native starches that are in-mill converted using either thermo-chemical or enzymatic techniques. These starches are mainly used for packaging papers/boards because of their cost effective strength enhancement.
- ❑ oxidised starches, starch ethers and starch esters used, mainly in fine papers despite their higher cost, because of their excellent solution stability and film-forming.
- ❑ cationic starches for their improved retention on broke repulping.

When broke containing size press-applied starches (usually nonionic or anionic) is recycled, these starches dissolve easily and contribute to the dissolved organics circulating at the wet end. Being biodegradable, these starches are probably the major nutrient source to wet end micro-organisms with their range of attendant problems and, if the starches are anionic, they will also contribute to anionic trash. Because of this, the use of more retentive (ie cationic) starches is becoming more important, particularly on machines where the recycling of broke would otherwise be the main source of wet end dissolved organics and/or on machines operating substantially-closed water systems due to their more substantial build-up of all dissolved solids.

When size press starch is added to a sized base paper (eg wood-free fine papers), the sizing of the paper is affected, but this depends on the starch distribution in the paper. As shown in the example at right, there are significant differences between the response of rosin and AKD sized papers to starch addition. The sizing of the rosin-sized paper improves, perhaps due to the weaker initial sizing allowing greater penetration of the starch into the body of the paper. The sizing of the AKD-sized paper deteriorates, perhaps due to the stronger initial sizing preventing penetration by the starch, which thus covers the sized surface. The addition of surface size (in this case, a styrene-maleic anhydride) improves the sizing of both papers, but particularly of the starch-impaired AKD sheet. For some applications, the presence of starch is an advantage as it enhances toner adhesion in some laser-printed papers (or rather it reduces the poor adhesion of papers sized with AKD) and it provides a receptive layer for rapid absorption of the ink's liquid phase (water) in ink-jet printing.



Source:Varnell at Pira Sizing Conference, London, 1997

Steric stabilisation

This phenomenon (also known as colloid protection) is utilised to stabilise colloidal dispersions and prevent particle aggregation. It is brought about by the adsorption of nonionic polymers onto particle surfaces and the resultant repulsion between inter-penetrating polymer chains extending from the surface. This type of stabilisation requires high polymer doses to give high surface coverage and for the polymer to have good water solubility. Aggregation occurs when the polymer solubility is reduced.

Steric stabilisation can be divided into two types, which are classified on the basis of their temperature dependence:

- entropic stabilisation (eg by nonionic polyacrylamide), in which aggregation occurs on cooling
- enthalpic stabilisation (eg with polyethyleneoxide), in which aggregation occurs on heating.

Steric stabilisation is utilised in the preparation of some papermaking additives such as styrene-acrylate surface sizes, but it is thought not to be important in at the wet end of most papermaking systems due to the absence of uncharged polymers of adequate chain length. However, there are two possible exceptions to this:

- where there are high concentrations of high molecular weight native (nonionic) starches

  In most situations, the starch concentration in unlikely to be high enough and, where it might be (ie on machines with very closed water systems, the starch is likely to be too degraded. However, there have been reports of improved particulate retention when pulp suspensions were pre-treated with amylase enzymes, the implication being that the enhanced water solubility of degraded starch allows it to desorb from the particle surface.
- pitch in unbleached mechanical pulps

  This is stabilised by the adsorbed galactoglucomannans, but this stability tends to break down when the pulp is bleached due to deacetylation which reduces their solubility, thus allowing the pitch to aggregate.

Stickies

Somewhat unfortunately, this is now a very well-known class of deposit-forming materials that have to be faced by nearly all mills based on post-consumer recovered paper. As well as the normal range of deposit problems in the wet end stock, untreated stickies retained in the paper form spots that can adhere to fabrics/rolls and also cause "stick-downs" (the adhesion of adjacent paper layers) due to melting in the drying section, which can lead to runnability problems at the re-winder. Although their chemistry is very different, stickies are analogous to the extractives in virgin pulps that cause pitch problems.

Stickie contaminants are present in many types of recovered paper as a result of the incorporation of adhesives during conversion of the paper/board to the finished article, such as in magazines and packaging products. Although the balance of adhesive types varies between the grades of recovered paper, they all fall into two main categories:

- contact or pressure sensitive adhesives

  These materials are tacky at ordinary temperatures and bond rapidly with the substrate with little applied pressure. Their chemistry is based on acrylates, polyvinylacetate, etc.

- hot melt adhesives

  These solvent-free adhesives are tacky only at elevated temperature and bond with the substrate on cooling. The chemistries used include ethylene vinyl acetate (EVA), ethylene ethyl acrylate (EEA) and styrene butadiene (SB) plus tackifying resins, waxes, antioxidants and plasticisers.

Some adhesives, mainly in the packaging sector, are associated with tapes, which are made from polypropylene (PP), polyvinylchloride (PVC) and polyethyleneterephthalate (PET). Stickies can also include materials from coated papers (both conventional aqueous coated and barrier-coated) that would by classed as "white pitch" when present on a paper machine using its own coated broke.

The stickies themselves are usually classified into two categories depending purely on their particle size rather than on their chemical character:

- macro-stickies which are larger than 0.1mm (100 µm) and are usually measured by a standard screening technique followed by image analysis to give a result in stickie area per unit mass of stock solids. Levels in incoming recovered paper are around 5000 mm^2/kg in deinking grades up to around 50,000 mm^2/kg at packaging mills making liner/fluting.
- micro-stickies, which are the smaller stickies (generally 1-100 µm) passing through the screen used for separation of macro-stickies. This fraction can be measured by concentration (eg by chemical aggregation) followed by solvent extraction/chemical analysis. Micro-stickies are generally not present as such in the incoming recovered paper, but are generated in the deinking or mechanical cleaning process as a result of the inevitable mechanical action on the stock.

This classification reflects the reality of the systems in mills where the objective is generally to remove macro-stickies by mechanical cleaning processes such as the various forms of screening (and flotation in deinking systems), whilst micro-stickies are not removed but treated chemically to stop them causing problems. Fine screening (eg 0.2mm wide slotted screens) is the most effective treatment for removal of macro-stickies, but the removal efficiency is always a compromise between maximising stock cleanliness and minimising fibre loss. Typical removals of macro-stickies in such systems are 80-90%.

Stickies can be controlled using the same hierarchy of techniques summarised generally for all deposit-forming substances and discussed elsewhere specifically for pitch and slime. In terms of stickie deposit problems, these are:

- ❑ selecting raw materials with the lowest possible content of stickie-forming materials

  This is somewhat impractical given the heterogeneity and uncertain content of many grades of recovered paper, but it would be good practise for all converters (and papermakers) to bear in mind the impacts of added materials for the future recycler of their product.

- ❑ so far as it is practicable, optimising machine operation (without chemical addition) firstly to minimise deposit-forming interactions and then to minimise deposition on surfaces.

  The most important element at this stage in the prevention process is to minimise the generation of the most troublesome micro-stickies by handling the stock as gently as possible (eg the use of high-consistency, drum-type pulpers) allied to the efficient, early removal of the intact macro-stickies.

- ❑ dosing of specific chemicals for control of micro-stickies.

  Chemical treatment can be applied not only to the papermaking stock, but also to the forming wire and/or the press/drying. In some extreme cases with poor stickie control, solvent cleaning (eg kerosene) has to be applied to the wire during machine shuts and web breaks in order to remove accumulated debris. There are several different chemical approaches, which are sometimes used in combination:

  - adsorption

    This approach is similar to the adsorbent treatment of pitch (with talc or bentonite), but is not as widely-used for stickie control. It must be combined with effective retention of the stickie-adsorbent combination in the paper.

  - charge adjustment or fixation

    This involves the early addition of low molecular mass, highly cationic polymers (such as a polydadmacs) and is somewhat similar to the technique used for the control of anionic trash.

  - surface stabilisation

    This uses a combination of dispersants and wetting agents such as nonionic or anionic surfactants.

  - detackification

    This is somewhat similar to surface stabilisation, but is aimed at changing the surface tackiness. Zirconium salts (eg acetate, nitrate) have a strong affinity for oxygen-containing groups such as hydroxyls and carboxyls and have been used successfully by some mills for detackification of stickies. Polymers with the correct hydrophile/lipophile balance can also work in a similar way, using the hydrophobic part for attachment to the stickie followed by some cross-linking via the hydrophilic part to enmesh the stickie. One of the latest materials used successfully for stickie control by detackification is a protein, the amphoteric and amphipathic character of which facilitates different sorts of interaction with stickie surfaces.

  - degradation

    This is based on enzymatic treatment with an esterase (an enzyme able to break down the ester linkage), for which there are at least two potential substrates within stickies - polyvinyl acetate and ethylene vinyl acetate. Empirical evidence from mill trials shows that stickie numbers are reduced by this treatment giving better machine runnability and reduced downtime.

Stiffness

This strength parameter is the resistance of paper to a bending force. There are various measurement techniques, one of the more common being the Taber method in which the sample strip is clamped at one end and the force to deflect the free end through 15° is measured (in mN.m). The Gurley method is similar except the strip is bent in both directions to give the average value. Stiffness is particularly important for packaging grades of paper, notably for container boards, for which there a number of specific functional strength tests such as the Concora test for fluting medium and various crush tests measuring compression resistance.

Stiffness is proportional to the cube of the paper's caliper meaning that the stiffness is reduced to one eighth of its initial value when the caliper is halved. In accordance with the well-known beam principle used in construction, stiffness is enhanced by having two strong outer layers around a weaker inner layer. This can be achieved in a multi-ply board by using a stronger pulp for the outer two plys and a weaker pulp for the middles and by forming a strong starch film on both sides of the paper.

Stoichiometry

This term refers to the relative proportions of two reacting substances. The proportions are stoichiometric when they are present at exactly the correct level to form the required product. For example, in the reaction of hydrogen and oxygen to form water:

$$2H_2 + O_2 \rightarrow 2H_2O$$

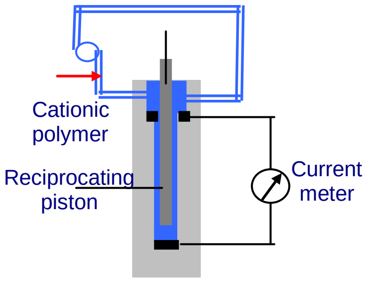
The stoichiometric quantities are 2 mole (4g) of hydrogen and 1 mole (32g) of oxygen to form 2 mole (36g) of water. One of the areas where stoichiometry is important is in charge-related polymer interactions, notably in relation to measuring anionic trash by a charge titration or actually controlling it in the papermaking system.

Strain

When a stress is applied to a body and the body deforms (eg compresses or elongates), the strain is the fractional change in its dimensions (length, volume, etc). If the stressed material is elastic, its strain returns to zero when the stress is removed. This is important to the strength properties of paper.

Streaming current

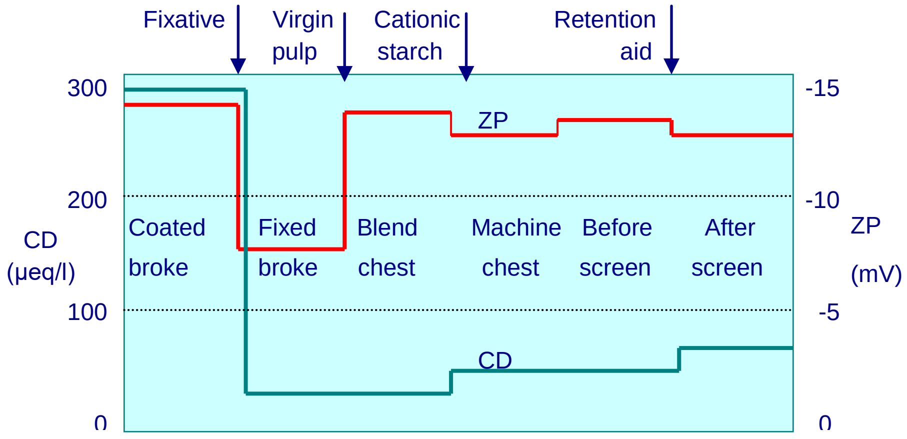
The device commonly known as a streaming current detector (SCD) is based on a similar principle to streaming potential as measured in a pad-forming system, but utilises a very different measurement set-up. The SCD technique was developed in the mid-1960s and comprises a Teflon piston that reciprocates at about 4 cycles/second within a Teflon chamber, which is filled with the liquid sample (see diagram at right). The action of the piston forces the liquid to flow up and down within the narrow annular space (about 0.5mm) between the piston and the wall. Particles and dissolved solids can be adsorbed on the Teflon surfaces and the relative movement of liquid and adsorbed charged substances generates a streaming current between the two electrodes at either end of the chamber.



The electrodes are connected externally via a meter and it is possible to construct a formula between this streaming current and the system characteristics to measure the zeta potential of the surfaces. As the shear within the chamber can be high (estimated at 10 sec^{-1} at the top of the cylinder to 1000 sec^{-1} within the annulus) and the flow not laminar, it seems dubious to attempt such calculations.

In practice, this becomes somewhat irrelevant as the main use of this device is to measure the cationic demand of the sample, not the particulate potential. In this mode (as shown in figure above), the sample is recirculated through the SCD unit whilst being titrated against a standard solution of cationic polymer. This further complicates what is actually being measured, but the volume of titrant to give a zero streaming current/potential is taken as a measure of the sample's cationic demand. The technique is most commonly applied to filtered or centrifuged samples, in which the only particles that might be present are of colloidal dimensions, so the measured value is the soluble or dissolved cationic demand, usually expressed in charge units (such as meq) per litre.

The SCD principle is embodied in many commercial instruments from suppliers such as BTG Mutek, Lasertrim, Chemtrac, etc, which have been used for many years for laboratory measurement of charged substances. These have proved very useful for research studies and were widely used on-line in the water treatment field for optimising coagulant addition. During the 1990s, a number of suppliers began exploring the on-line use of SCD units in papermaking for stabilising the wet end cationic demand from anionic trash. There are now several SCD devices on the market for on-line application (from the above companies plus Metso Automation), all being based on the same operating principle as the laboratory systems described above, but where an important component of the system is the provision for regular cleaning of the sensor module.



CD = online cationic demand by titration of filtrate with polydadmac
ZP = zeta potential of fines by off-line electrophoresis

Data from Mutek paper at Pira Sizing Conference, Barcelona, 2000

A number of mills have installed SCD units on-line as part of wider wet end on-line systems, some for monitoring only, but increasingly for control as well. Results from one on-line application of Mutek's SCD unit illustrates perfectly the benefits from this measurement (see figure above). This is for a coated fine paper machine, where the main source of anionic trash is the coated broke, which is treated with a cationic polymer (fixative) with the precise dose being controlled by the on-line cationic demand measurement. As is very clear in the above data, the cationic demand is effectively neutralised by the fixative, but the particulate charge remains negative so that it can still adsorb other cationic additives such as the starch and retention chemicals. Without this controlled neutralisation early in the system, the anionic trash would severely interfere with the performance of these chemicals.

Streaming potential

This is one of the four electrokinetic techniques used for measuring the zeta potential of particles. It differs from electrophoresis in being applicable to the whole sample (not just the fines fraction) - see this comparison of electrophoresis of fines versus streaming potential of the whole sample for a bleached chemical pulp. In this method, the particulate solids are formed into a pad by filtration and the liquid phase passed through it. The difficulty in using this type of device centres on the need to achieve uniform, reproducible plug formation to give either a measurable potential difference or streaming current:

$$\text{Streaming current, } I = ZP.D.P.\ f\,(\text{cell+plug})/\eta$$

$$\text{Streaming potential, } V = I/C$$

where D = dielectric constant of water, P = applied pressure
f (cell+plug) = constant dependent on the characteristics of the cell and plug
η = viscosity of water, C = conductance of water.

There are a number of commercial laboratory-based instruments (Brookhaven Instruments, BTG Mutek) as well as for on-line monitoring (Innomatic, Paper Chemistry Laboratory, Chemtronics) using this principle.

Strength

Adequate strength is a fundamental requirement for all papers, but the key strength parameter varies with grade. Strength parameters are usually measured as a force in Newtons, but the precise unit depends on the actual force being measured. Paper strength increases with the grammage of the paper, so the strength term is often normalised to remove this contribution by simply dividing the measured value by the grammage to give an index. Strength tests are used for measuring some aspect of the body strength of paper or its surface strength.

There are four commonly-used indices for body strength - burst strength, tensile strength, tear strength and stiffness with folding endurance also being important for some papers (eg banknotes). These strength characteristics of paper are normally measured when the paper is in a dry state (ie its dry strength), but, sometimes, there is a requirement for papers that remain strong when moist or wet. This is referred to as wet strength and can be measured simply by pre-wetting the paper for a certain time. The strength of the paper web itself is important in terms of process runnability during the various phases of water removal and this is referred to as the wet web strength.

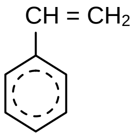
When paper is dry, its strength is a function of the strength of individual fibres and of the fibre network within the paper web, the latter being determined by the physico-chemical interaction between the fibres (and fines) at the wet end. The main technique to maximise the strength properties of fibres is refining, which brings about changes in fibre length and the extent of fibrillation. This leads to increased fibre flexibility and fibre surface area available for bonding. Whilst the main strength properties such as tensile and burst strength are improved by refining, tear strength generally decreases due to fibre shortening. The closer, more uniform fibrous structure also leads to better formation, which further improves paper strength and to increased sheet density, which gives lower bulk, porosity and opacity. Before the paper is formed, however, refining generates fine particles, which impair wire retention and water removal. The dry strength of paper can be enhanced through the use of chemicals (dry strength additives), which can be used instead of or in addition to refining.

Stress

A stress is a force applied to a body and normally has the same units as pressure, eg N/m^2. The tensile strength of paper is not usually expressed as the stress at failure, but as the force at failure per unit width, eg N/m. For an elastic material (ie one where the strain reverts to zero when the stress is removed), the ratio of stress:strain is the modulus of elasticity, eg Young's Modulus when the strain is the change in length, bulk modulus when it is the change in volume and rigidity modulus when it is a shearing force. A Newtonian liquid is not elastic as an applied stress results in flow, but there are some non-Newtonian liquids (visco-elastic fluids) that do store some of the applied force in an elastic form.

Styrene

This chemical (formula at right) is never found in papermaking in this simple form, but is polymerised with other monomers to form two classes of papermaking chemical:

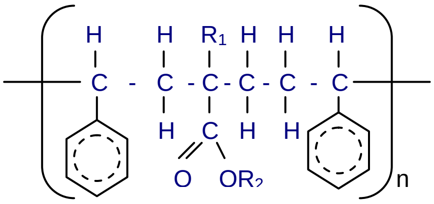


- surface sizing agents where it is polymerised with maleic anhydride, maleic anhydride esters, acrylic acid or acrylic esters
- coating binders where it is polymerised with butadiene or acrylates.

Polystyrene itself is present (unwantedly) in many papermaking systems using recovered paper in the form of polystyrene granules from their use as packaging fill.

Styrene-acrylate ester (SAE) co-polymers

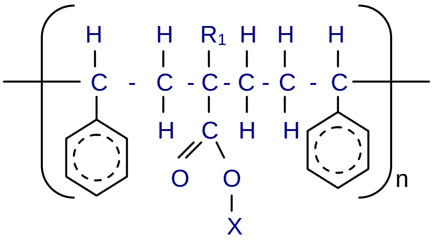
Co-polymers of styrene and acrylate esters (typical formula at right, where R_1 = H for acrylic acid and CH_3 for methacrylic acid and R_2 is also an alkyl group) are used for two distinct applications in papermaking:



- in the form of a latex as coating binders. Although they have lower binding strength than SB latices, they give better light fastness, gloss and ink absorbency.
- as surface sizing agents, which are a development from the water-soluble styrene-acrylic acid sizes. They are more commonly used today due to their greater efficiency and freedom from foaming problems. asa

Styrene-acrylic acid (SAA) sizes

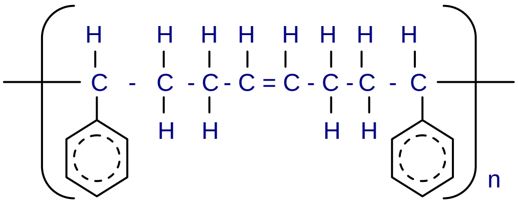
Co-polymers of styrene with acrylic acid or its derivatives are used as sizing agents for surface application and are most commonly being added with starch at the size press. In contrast to the styrene-acrylate co-polymers, these are solution polymers (typical formula shown at right although the relative proportions of the two components do vary considerably) where the X group is varied to give the molecule different charge/solubility characteristics:



- an anionic charge where X is simply a cation (ie the salt of acrylic acid) or where it contains a sulphonate group (to give it wider pH and ionic stability)
- a cationic charge where X is typically a nitrogen-containing derivative of the ester.

Amphoteric products are also possible by using mixtures of acrylate derivatives. The charge of the size is important in relation to its compatibility with other size press components (avoiding wherever possible additives of opposite charge) and with any water-soluble materials extracted from the paper web. Although styrene is the most common hydrophobic component, acrylate esters (as used in styrene-acrylate latices) may also be used for this purpose and these may be referred to just as acrylate-based sizes.

Styrene-butadiene (SB) latex



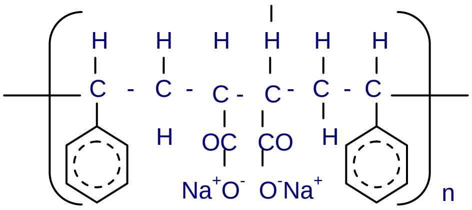
Co-polymers of styrene and butadiene (see typical formula at right) are used as coating latices. They are also used as contact adhesives in the conversion of some paper products. As styrene homo-polymers are hard and inflexible (glass transition temperature = +100°C) and butadiene homo-polymers are soft and flexible (glass transition temperature = -100°C), styrene and butadiene can be co-polymerised over a wide range of styrene-butadiene ratios to give products of varying flexibility and softness.

The styrene component of the coating latex enhances properties such as gloss and varnish holdout, whilst the butadiene component is good for wet rub resistance and a balanced level of both monomers is optimal for pick resistance. As a consequence of this wide range of product characteristics, they are the most common type of latex used as a coating binder. Typical formulations contain 50-60% styrene, 40-50% butadiene and up to 10% of a carboxylic acid modifier to confer better colloidal stability with a total solids content of 40-55%. The SB latex dispersion is fairly monodisperse with a particle size distribution within the range 100-200 nm. Even within this narrow range, particle size affects coated paper properties with smaller particles giving higher binding power, but suffering from increased viscosity.

Styrene-butadiene latices can cause problems in wet end chemistry:

- ❑ in the form of white pitch from SB latices in coated broke
- ❑ in the form of stickies from SBR latices in recovered paper.

Styrene-maleic anhydride (SMA) sizes



These were amongst the first type of sizing agents developed largely for application at the paper surface rather than at the wet end. They are co-polymers of styrene, which provides the hydrophobic character and of maleic anhydride, which provides the water solubility. The co-polymer is reacted with sodium or ammonium hydroxides to form the water-soluble salt (see formula at right for sodium salt). The anionic charge density is typically 3-4 meq/g for a 1:1 polymer The water-solubility imposes limits on its application due to precipitation at acid pH and in the presence of electrolytes and cationic substances. For these reasons, the use of polymer dispersions such as the SAE sizes is often preferred.

The performance of SMA sizes is dependent on the nature of the carboxylic acid groups (salt or ester), the ratio of the two monomers and the overall molecular mass of the polymer. A common form of SMA sizes is the ammonium salt, in which one of the carboxylic acid groups is converted to an amide ($-CONH_2$) group, as this is more hydrophobic than the sodium salt. Increasing the styrene:maleic anhydride ratio makes the size more hydrophobic, but at the expense of poorer film-forming ability. Sizing tends to increase with molecular weight, but the coefficient of friction shows the reverse trend. As well as sizing, these chemicals have been used to overcome surface slippiness problems with some papers sized with AKD at the wet end (see this example for its effect on sizing AKD- and rosin-sized base papers).

Substantivity

This term is synonymous with adsorption, but its use is largely restricted to discussion of dyes and brighteners.

Sugar

This is a common term for carbohydrates that contain 1 to 4 saccharide units and these are divided into monosaccharides and oligosaccharides.

Sulphate

This is a fairly common anion (SO_4^{2-}) that may be present in the papermaking system from various sources:

- ☐ the fresh water where it is normally associated with sodium/potassium salts or calcium/magnesium salts (permanent hardness)
- ☐ the addition of alum or sulphuric acid
- ☐ the addition of calcium sulphate as a filler or coating pigment.

Apart from its contribution to electrolytes levels, sulphate is also significant as a source of energy for sulphate-reducing bacteria and as a divalent anion that can interact with cationic species such as alum. When calcium carbonate (in recovered paper or mill broke) is being deliberately neutralised with sulphuric acid, sulphate can precipitate as calcium sulphate, but this only happens on paper machines with very closed water systems. As with all soluble ions, the sulphate concentration on the paper machine depends on its input load and the degree of water closure (see these values for several machines with fully-closed water systems).

The sulphate level in paper products is sometimes measured as it can be reduced to sulphide, which could tarnish metal surfaces with which some papers come into contact. Sulphate can be measured on waters or paper extracts by ion chromatography or by titration (or precipitation at higher levels) with barium salts.

Sulphate pulps

This is an alternative term for Kraft pulps.

Sulphate reduction

Most papermaking systems contain measurable levels of dissolved sulphate ions so there is always the possibility of this being reduced microbiologically to sulphides. This is an example of one of several ways in which different bacteria can change the chemistry of substances within the papermaking system. The sulphate-sulphide redox couple can be most realistically written as:

$$SO_4^{2-} + 9H^+ + 8e^- \leftrightarrow HS^- + 4H_2O \text{ where } E_H^o \text{ (redox potential) } = +0.24 \text{ volts at } 25^oC$$

As the pH becomes less acidic, the actual redox potential of this couple becomes negative indicating that sulphate can only be reduced to sulphide under strict anaerobic conditions at around neutral pH. This tends to occur well away from any water:air interface, such as within attached slime layers in pipes and tanks. Thermodynamically, sulphate can be reduced to sulphide by hydrogen gas without the agency of bacteria, but this does not occur due to slow kinetics. Several different species of bacteria are able to reduce sulphate to sulphide, but the most common is *Desulphovibrio desulphuricans*.

Sulphide

Sulphide (S^{2-}) s a simple anion of sulphur, which is very important for lignin removal in the Kraft pulping process, in which it is formed in situ by the reduction of added sodium sulphate. Sulphides are not present in the papermaking system through any deliberate action, but may be generated by anaerobic sulphate-reducing bacteria. The sulphide can exist in any of the following forms depending on the position of the various equilibria:

$$H_2S\text{ (g)} \overset{k_H}{\leftrightarrow} H_2S\text{ (aq)} \overset{k_1}{\leftrightarrow} H^+ + HS^- \overset{k_2}{\leftrightarrow} S^{2-} + H^+$$

In neutral pH waters, the dissolved sulphide will be a mixture of aqueous H_2S and the bisulphide ion (HS^-) as $pK_1 = 7.1$ and $pK_2 = 14$ at 25°C ($pk_H = 1$). Some of the sulphide is precipitated as ferrous sulphide around the sulphide production site close to the metal-slime surface, but, once the sulphide-containing water is exposed to the atmosphere, the equilibria will be displaced towards the left and most of the sulphide released as hydrogen sulphide gas.

Sulphite

This anion (SO_3^{2-}) may be present at the wet end of some paper machines due to the addition of sodium sulphite or sodium hydrosulphite. The anion will actually be present in the form of a mixture of bisulphite and sulphite ions as the pk_2 value for sulphurous acid is about 6.9 at 25°C ($pk_1 = 1.8$). Concentrations of sulphite/bisulphite up to about 100 mg/l have been measured on newsprint machines using hydrosulphite bleached mechanical pulps. There should be no significant sulphite residuals in sulphite pulps with the possible exception of NSSC pulps. Sulphite is oxidised by dissolved oxygen to sulphate, but this reaction can be rather slow in the absence of suitable (metal ion) catalysts.

Sulphite pulps

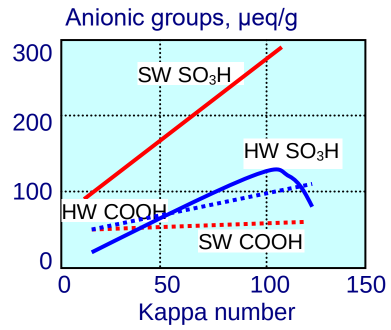
Pulping by one of the various forms of the sulphite process used to be the dominant chemical pulping process globally until about the middle of the last century. It has since declined in favour of the Kraft process for a combination of reasons:

- the complexity/difficulty in recovering the cooking chemicals and related environmental problems
- its relative unsuitability for pulping softwoods compared to hardwoods
- the lower fibre strength compared to that of Kraft pulps.

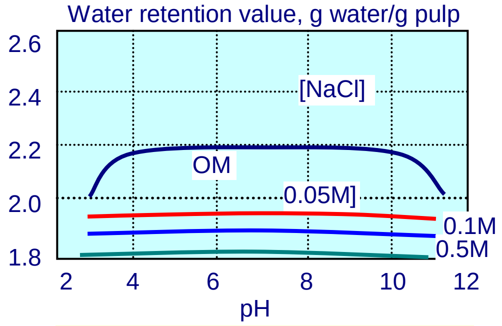
The above comments mainly apply to the original calcium-base process, there having been a number of process developments over the years to use sulphite with other base cations (sodium, magnesium or ammonium) at different pH levels:

- original acid sulphite process at pH 1-2 with a high proportion of free sulphur dioxide, using any base, but most commonly calcium. Because of the strongly acidic pulping conditions, unbleached pulps of this type have a very low level of lignin and are thus very easily bleachable producing a very clean bleached pulp. These pulps are still used as dissolving pulps for rayon/chemical manufacture.
- bisulphite process at pH 3-5 with a low proportion of free sulphur dioxide, using any base except calcium
- neutral/alkaline sulphite process at pH 7-10 with no free sulphur dioxide, normally with sodium base, such as the neutral sulphite semi-chemical process.

During sulphite pulping, the lignin dissolves as lignosulphonate in the pulping liquor towards the end of the digestion. This substantially increases the content of anionic substances above that from the natural carboxyl groups. As the charge character of unbleached sulphite pulps is dictated by the content of retained lignosulphonate, the pulp's Kappa number can be used as a reasonable indicator of its charge content (as shown at right, where the charge is measured as the ion exchange capacity). For both hardwood (HW) and softwood (SW) sulphite pulps, the carboxyl charge becomes more significant at the low Kappa numbers more typical of bleached pulps. The wood hemi-celluloses are easily hydrolysed to simple sugars under acid conditions, but those with remaining carboxyl groups lose their charge below about pH 3.



Source: Lindstrom, Nordic Pulp and Paper J., 1992, 4, 181-192.



Source: Lindstrom, Nordic Pulp and Paper J., 1992, 4, 181-192.

As shown at left, the swelling of an unbleached sulphite pulp reflects the different charge characteristics of the lignosulphonates and anionic hemi-celluloses. The baseline swelling of the pulp is quite high because of the sulphonate groups that are fully ionised throughout the pH range. With no added electrolyte, the swelling increases between pH 3-5 as the carboxyl groups ionise but, at low and high pH, the added acid/alkali acts as an electrolyte to shield the charges from one another. The effect of added electrolyte shows that, in most papermaking systems, there should be enough ions present to reduce pulp swelling significantly and to negate any effect of pH.

The final levels of lignin and hemi-cellulose in unbleached sulphite pulps are about 4 and 15% respectively. In terms of particulate contaminants in sulphite pulps, removal of acidic extractives is limited, so the content of pitch in the unbleached pulp (1-2%) is much higher than in unbleached Kraft pulps (<0.5%). Oxalic acid is generated during the pulping process and sulphite pulps are thus prone to problems from precipitation of calcium oxalate.

Sulphonates

This functional group has similarities with bisulphite, both having the simple formula HSO_3^-. The difference is that the linkage in sulphonates is via the sulphur atom (- SO_3H) whereas it is via one of the oxygens (- OSO_2H) in bisulphites. In papermaking, sulphonates occur as residual substances in some chemimechanical and sulphite pulps in the complex form of highly anionic lignosulphonates and sulphonation is used to improve the solubility of dye and brightener molecules.

Sulphur

This element follows oxygen in Group 16 of the Periodic Table and occurs naturally as a yellow solid and is present in several papermaking raw materials or their reaction products:

- as the sulphate anion, which originates from fresh waters and any added alum
- as the sulphite anion, which originates from any added sodium salt
- as the thiosulphate anion, which originates from the breakdown of hydrosulphite ions
- as lignosulphonate residues in sulphite pulps
- as the sulphonate anion in some dye and fluorescent brighteners
- as the sulphide anion through microbial reduction of sulphate
- as various organo-sulphur compounds used as biocides.

Sulphuric acid

This is a very strong acid with pK values for its two ionisation constants of -3 and +2. Solutions of sulphuric acid thus contain no free sulphate ions, only protons and bisulphate ions. However, at normal wet end pH values (ie pH > 4), the anion will always be sulphate, the presence of which is not desirable due to its availability to sulphate-reducing bacteria and the possibility that it will reduce the charge of cationic additives. Concentrated sulphuric acid (ca 98% acid) has a very high heat of hydration and dilute solutions should always be prepared by adding the acid slowly to the requisite volume of water and never in the reverse order.

Sulphuric acid has various uses in papermaking:

- most commonly for pH control, ie usually to adjust the pH from around neutral to an acidic level, eg for sizing with rosin or wet strengthening with UF or MF resins
- in water treatment for the conversion of temporary hardness bicarbonates to permanent hardness as sulphates
- in the manufacture of vegetable parchment.

Super-calendered paper

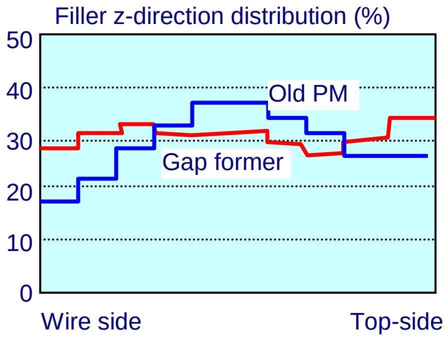
This is a grade of wood-containing paper, the name being derived from the use of special on-machine calenders to give the paper a smooth surface finish. There are a number of SC grades (SC-A, SC-B, SC-C, SC+) depending on the balance of raw materials and paper specification. SC papers are normally made with no surface application, but some improved SC qualities may be surface-treated to try to match the printing quality of LWC papers.

There are three main constituents in SC papers:

- mineral filler, the content of which increases from SC-C (5-10%) through SC-B (10-15%) to SC-A (20-35%) as the printing quality of the paper surface improves to give improved smoothness and gloss. The filler is traditionally a kaolin clay due to its good response to calendering, but special precipitated grades of calcium carbonate are also now being used to give a gloss finish and resist the slightly acidic wet end. The kaolin clays tend to be quite coarse in order to minimise adverse effects on strength and machine runnability.

- ☐ bleached Kraft pulp, the content of which increases in order to maintain adequate strength as the filler content rises
- ☐ mechanical pulp, the content of which changes in response to the requirements for filler and bleached chemical pulp as the SC grade changes. Over the last 10 years or so, deinked pulp has begun to be used to replace part of the mechanical pulp.

The other main additive is wet end cationic starch for strengthening, particularly on the highly-filled SC-A grades. Like newsprint, SC papers are made to a particular brightness specification, but this tends to follow the filler content and goes up to about 72% ISO. Product grammage is in the range 40-60 g/m^2. SC paper machines are very fast (up to about 1800 m/minute) and generally employ gap-formers to give an even-sided, well-formed product.



The key issue for wet end chemistry is clearly to achieve a reasonable single pass retention for the fines (which can easily reach about 50% of the thick stock particulate solids) combined with good paper formation and an even-sided structure. An example is shown at right for a machine re-build in the mid-1990s, where a gap former replaced an older, slower machine. The new machine gives an excellent z-distribution of filler for the highly-filled SC-A grade, even though the single pass retention of the total furnish is only 45-50%. The retention aid chemistry to cope with these conditions would typically be based on dual polymers with a highly cationic low molecular mass polymer for charge neutralisation followed by a polyacrylamide for fines aggregation.

Surface application

This is the alternative way of adding non-fibrous raw materials to the pre-formed paper web either on-line as part of the paper machine system or in a separate off-line operation. In this document, it is considered to be part of a paper machine's dry end chemistry. Surface application is not carried out on all paper machines, there being many grades of paper that contain only wet end additives, eg newsprint, tissues, towels, etc.

There are basically three different techniques for applying either a suspension or solution of chemicals to the paper surface:

- ☐ spraying the fluid onto the moving paper web prior to drying
- ☐ impregnation by contacting the dry paper web with the liquid, most commonly in a size press or, on machines with calenders, at the water box, both techniques allowing the paper web to imbibe what is commonly a solution rather than a suspension. This process always forms part of the paper machine system.
- ☐ coating using various types of application head in an off-line or on-line process .

The chemical nature of surface-applied materials varies with the type of applicator and each is described under the above headings. It is important to recognise that surface-applied chemicals suffer none of the uncertainties relating to retention that wet end additives have to contend with, but that a significant fraction of surface-applied chemicals enters the wet end system through the recycling of broke and the re-use of recovered paper. Because of this, it is important that the selection of surface-applied chemicals should consider their potential effects on wet end chemistry and, wherever practicable, avoid the use of surface-applied chemicals that could cause wet end problems.

It is equally important to recognise that chemicals in the base paper can affect the process of surface application through their being extracted during passage through the applicator. As the retention time of the paper web in the applicator is very low, this problem is mainly restricted to the more easily water-soluble chemicals such as electrolytes and those processes with longer retention times such as the traditional puddle-type size press. The severest problems tend to occur on size press machines with a very closed water system at the wet end as this tends to lead to high retention of dissolved materials. Acidic conditions in the applicator could also lead to dissolution (and foaming) of calcium carbonate from a filled base paper and should obviously be avoided.

Surface energy/tension

This is described under the more generic heading of interfacial energy. The surface energy or tension is best reserved just for interfacial energy or tension between a material and air.

Surface properties of paper

There are a number of miscellaneous paper properties that depend on certain characteristics of the paper surface:

- its surface energy in relation to sizing and liquid absorption effects
- smoothness, which is very important for some grades of paper such as printing papers
- surface strength, which is important for the runnability of papers during conversion and/or use
- friction, which is important during winding, sheet feeding, converting and stacking operations
- softness, whose importance is restricted to just tissue and towel grades.

For all these properties, it is important to recognise that the two sides of a paper sheet are rarely identical in terms of their composition (ie the paper is two-sided to some degree) and may therefore have quite different values for these measured properties. These differences arise from the nature of the filtration process in forming the paper web, where finer particles are likely to be concentrated on the topside of the paper, particularly when the single pass retention of the fines is low (see examples under z-distribution).

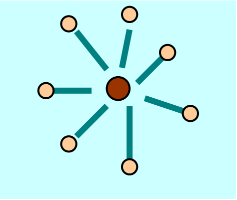
Surface strength

The paper surface, notably the topside, may accumulate materials that are poorly-bonded to the body of the paper. This can result in the picking (pulling off) of pulps fibres or the linting of fillers during pressing/drying and printing (when it may be referred to as dusting). Sometimes, the fibres do not leave the paper surface, but are lifted by abrasion against another surface and the ability of a paper to resist this is termed scuff or rub resistance.

The main technique for quantifying surface strength is the Dennison Wax Pick test, which involves the application of a series of waxes with graded adhesive properties to the paper surface. The (highest) number of the wax that does not remove any paper material when it is pulled off is the Dennison Wax Pick value. A set of technique which more closely simulate the printing process are the IGT tests for dry and wet pick resistance. Surface strength of an uncoated paper can be enhanced by chemical treatment at the size press, most commonly with starches.

Surfactant

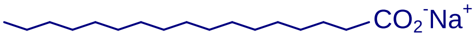
A surfactant is a surface active agent, meaning that it tends to accumulate at a surface or interface. Surfactants are amphipathic as they possess both hydrophobic and hydrophilic groups, the relative proportions being quantified by the HLB number. There is usually adequate hydrophilic character to make surfactants soluble in water, but the hydrophobic part of the molecule would prefer not to be exposed to water and, above a certain concentration, surfactants form micelles in which the molecules form aggregates with the hydrophobic ends clustering together (see picture at right). This allows them to hold hydrophobic solids within the micelle, thus effectively "dissolving" them.

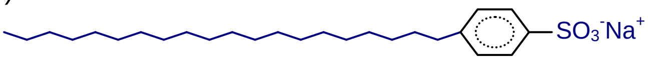


For the same reason, surfactants prefer to adsorb on a particle surface (particularly if the surface has some hydrophobic character) with their hydrophobic ends adjacent to the surface and their hydrophilic ends pointing outwards, thus allowing the surface to be held dispersed as a stable water suspension. In a similar way, surfactants also concentrate at the air-water interface and can thus stabilise entrained gases as a foam.

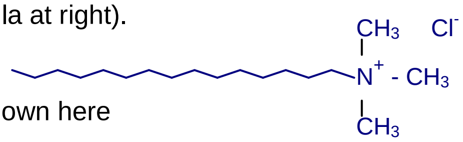
Surfactants are usually classified in accordance with their charge character:

- anionic surfactants such as sodium stearate which is derived from natural fats (see right) and synthetic chemicals such as sodium dodecylbenzene sulphonate (see formula at right).



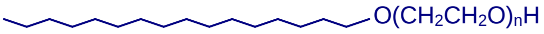


- cationic surfactants such as cetyltrimethylammonium chloride, as shown here



$$\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{N^+}} - CH_3 \quad Cl^-$$

- nonionic surfactants such as the alcohol-ethoxylates, as shown here



Surfactants have a range of possible applications in papermaking:

- incorporation in cleaning agents, which may be acidic or alkaline
- the formulation of creping chemicals
- as emulsifiers with sizing agents
- as absorbency aids to enhance fibre wetting
- as foam control agents, but using molecules that are more hydrophobic than those causing the foam.

Substances with surface active properties can get into the papermaking system through other materials, notably in the form of saponified resin acids from virgin pulps, deinking surfactants and soap residues in deinked pulps. Talc filler also has some surface active properties because of its part-hydrophobic character.

Swelling

In papermaking, this term refers to the ability of pulp fibres to expand when exposed to water and is important both during and after papermaking. In the latter case, the moisture content of the dried sheet adjusts to changes in the relative humidity of the surrounding atmosphere and this affects the dimensional properties of the paper. Swelling of pulps is measured either by inverse solute exclusion, in which case the measured value is the fibre saturation point (FSP), or by measuring the water remaining in the pulp after a standard centrifugation, which is called the water retention value (WRV). Both terms have units of g water/g dry fibre.

Pulp swelling opens up existing pores in the fibre wall, which are classified into two types:

- ☐ micro pores, which have a diameter of 1-4 nm and are located in the amorphous regions of the fibre wall
- ☐ macro-pores, which have a diameter of 30-80 nm and are believed to originate from dissolution of lignin and hemi-cellulose during pulping.

As in the FSP test procedure, pore size is important in relation to the ability of papermaking chemicals of different molecular sizes to gain access to the internal fibre surfaces.

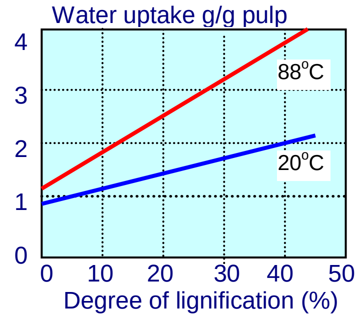
At the wet end, pulp fibres start to swell during the initial slushing stage as water penetrates the amorphous (non-crystalline) regions and forms hydrogen bonds with the hydroxyl groups on the accessible cellulose molecules. This is an exothermic process and it improves the papermaking value of the fibres as they become more plastic/flexible and better able to conform to one another during later drying. There is some ordering of the water molecules adjacent to the fibre surface, which leads to it having a somewhat higher density than the bulk water. However, the penetration of water into and its uptake by the fibrous matrix depends on the latter's chemical composition as this affects the energy of the interface with water. There is a significant difference between the wettability of mechanical and chemical pulps as the presence of lignin reduces the surface energy of fibres, whilst the hydrophilic hemi-celluloses have the opposite effect. Further changes in fibre swelling occur during pulp refining as the external and internal structure of the fibres are developed.

Our understanding of the mechanism of fibre swelling is based on treating the fibre wall like a polyelectrolyte gel and most practical observations support this premise. The degree of fibre swelling reflects the balance between the expanding forces and the force opposing expansion. The latter is simply the elastic tensile strength (or modulus) holding the components of the fibre wall together, which has been shown to increase with the pulp's lignin content. The expanding force is a mixture of two terms, but both can be related to the osmotic pressure resulting from the difference in concentration of ions between the accessible and non-accessible water (Donnan equilibrium). Swelling thus increases with the quantity of anionic charged groups associated with the pulp.

The nature of the counter cation also affects swelling, which increases as the cation changes from Al^{3+} to H^+ to Ca^{2+} to Na^+. The ability of pulp fibres to swell thus depends not only on the chemistry of the pulp, but also on the chemistry of the process water used for pulp dilution. A higher electrolyte concentration in the pulp dilution water opposes swelling as it reduces the osmotic pressure driving force.

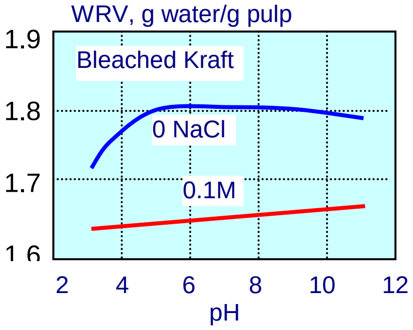
The swelling behaviour of mechanical pulps is restricted by their high lignin content. Their water retention value is typically around 1 g water/g pulp, about half of that for chemical pulps. The stiffening effect of the lignin may be partially overcome by increasing the content of anionic groups, eg by peroxide bleaching or by sulphonation. This example shows the improvement in swelling brought about by alkali treatment of two mechanical pulps and their consequent increase in pulp anionicity due to hydrolysis of ester linkages.

Temperature has been shown to affect fibre swelling, as illustrated at right for a pulp delignified to varying degrees with sodium chlorite. As temperature had no effect on the swelling of pure cellulose, this effect appears to be due to a combination of lignin softening and disruption of hydrogen-bonded cohesive forces in the fibre wall.



Source: Lindstron in Nordic Pulp Paper Research J., 1992, 4, 181-192.

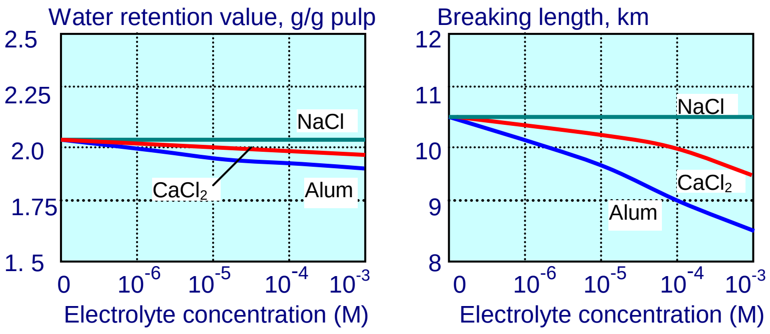
As the above figure also indicates, the swelling of pulps increases as lignin is removed. At any particular lignin level, the swelling is strongly influenced by the pulp's content of residual charged substances (for the reasons explained above). In comparison to bleached chemical pulps, unbleached pulps have a relatively high content of anionic substances so they swell readily in the absence of electrolytes (see these examples for unbleached Kraft and unbleached sulphite pulps). These examples also show how the swelling depends on pH, as this influences the ionisation of charged groups and how swelling is reduced in the presence of added electrolytes and at low and high pH due to the electrolytic effect of high acid/alkali doses. The swelling of unbleached Kraft pulps differs from that of unbleached sulphite pulps due to the presence of acidic groups with higher pK values, eg lignin phenolic groups.



Source: Lindstrom, Nordic Pulp Paper Research J., 1992, 4, 181-192.

In line with their low lignin content, bleached Kraft pulps show good swelling characteristics, which depends on their total charge content (as shown here). This study showed that the swelling of birch hardwood pulps was more sensitive (than softwood pulps) to the positive influence of total charge content and to the negative influence of electrolytes. In a separate study (see figure at left), the small increase in swelling with raised pH is consistent with this undefined bleached Kraft pulp probably having been chlorine bleached and thus having a very low carboxyl content.

Swelling is usually considered desirable as the increased flexibility of the pulp fibres allows them to conform to one another more easily and thus increase the strength of the paper. One study has investigated the relationship between pulp swelling and paper strength for a bleached sulphite pulp with a low content of anionic groups. From the figures below, it is clear that, although the drop in swelling with increased electrolyte level is quite small, there is a significant loss of paper strength.



Source: Shehanev in Paper Technology Industry . 1981. 22. 4. 181-192.

However, it should be noted that there are two undesirable consequences of fibre swelling:

- the ease of water removal during pressing is impaired due to an increase in the water-holding capacity of fibres (see this example).
- the dissolution of organic substances is increased as the size of the internal pores expands, thus allowing hemi-celluloses to diffuse through the fibre wall (see refining)

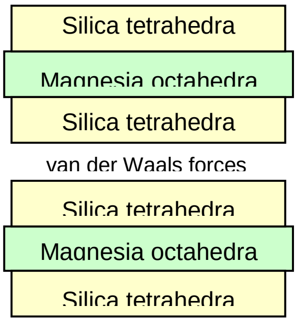
Symplex

This is the name for the complex formed between dissolved polymers having an anionic charge on the polymer chain and polymers having a cationic charge on the polymer chain, ie between anionic trash and added cationic chemicals (see charge interactions).

Synthetic pulps

This class of pulps is not very common in papermaking and is mainly used in speciality grades such as tea-bag and filter papers. As these pulps are not cellulosic in nature, they do not bond well with one another or with cellulosic fibres so it is usually necessary to add binders. Examples of synthetic pulps are glass fibre used in filter papers and thermo-plastics such as polypropylene in heat-sealable tea-bags.

Talc

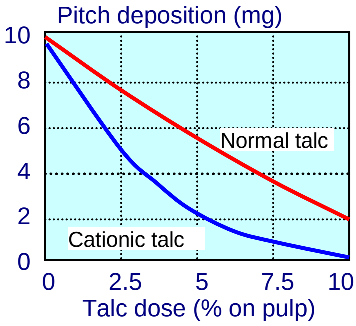


Talc is a platy magnesia-silicate mineral from the clay group with the formula $Mg_3Si_4O_{10}(OH)_2$ and the structure as shown in a simplified form at right. In the magnesia layer, the magnesium ions are surrounded by four oxygens (from the silica layers) and two hydroxyl groups. Talc is easily delaminated due to the weak inter-plate van der Waals forces and is therefore very soft (Moh scale 1-2 depending on the level of impurities). It has a very low ion exchange capacity (<0.02 meq/g, ie much lower than kaolin or bentonite clays) due to its well-balanced ionic composition. Its most interesting property is its surface characteristic of having a very low energy (hydrophobic) face (interfacial energy 35-40 mJ/m^2) combined with hydrophilic edges (due to the hydroxyl groups in the protruding magnesia layer). The zeta potential of talc is weakly negative (-2 millivolts) at normal papermaking pH levels.

It is most commonly produced by a combination of dry grinding and classification to give different particle size distributions, notably a coarse grade with a mean particle diameter of about 10 µm and a fine grade with a mean particle diameter of about 1.5 µm. Talc has several applications in papermaking:

- for the control of pitch and stickies

  This is the biggest general application for talc with typical addition rates of about 1% on pulp. Talc addition is probably the most widely-used technique for pitch control due to its simplicity, but it is very important to secure good single pass retention of the talc/adsorbed pitch as talc's amphipathic character could contribute to foam stabilisation if levels built up. In recent years, modified talcs have been introduced to give better pitch adsorption at neutral pH (see example at right for a cationic talc product).



Source: Biza in Paper Technology, 2001, 42, 3, 22-24.

- as a wet end filler and coating pigment

  This is mainly restricted to those regions where it occurs naturally, eg Finland. Its properties as a filler are compared with other fillers under the following headings - brightness, light-scattering and refractive index. Due to its part-hydrophobic character, talc can be poorly-bonded to the fibre surface and hence prone to dusting.

Tapioca starches

This type of starch is not as common in papermaking as the three main types (potato, corn/maize and wheat). Tapioca starches have a higher amylopectin content even than potato starches and contain no fatty material (see this table for comparison with other starch types). They have a quite large granule size with a mass average of about 15 µm and are round in shape, but with truncated ends.

TCF

This is an abbreviation for totally-chlorine free in relation to pulps or pulping processes.

Tear strength

This strength parameter is the paper's resistance to being ripped in one direction and is measured by a pendulum-type tester. The value is expressed in mN or, when normalised, as the tear index in mN.m^2/g. The tear strength may be measured at the edge without an initial tear (the edge tear strength) of after initiating a small tear (the internal tear strength), the latter being less than the former. As with tensile strength, the tear strength depends on the tear direction with the CD-tear strength being greater than MD-tear strength. Tear strength is particularly dependent on the content of long fibres in the pulp, so refining beyond a certain level (whilst the tensile strength is still increasing) reduces tear strength due to fibre shortening.

Temperature

Temperature affects many processes in the papermaking system due its effect on rates of chemical and microbiological reactions. Uncontrolled variations in temperature mainly occur at the wet end of the paper machine as the temperature during surface application is usually controlled in some way due to its effect on the rheology of the applied aqueous systems. The highest temperatures are experienced in the drying of paper and this is very important for some aspects of dry end chemistry.

At the wet end, the temperature of the fresh water establishes the baseline temperature of the system, which varies with season, but this variability is more pronounced for surface waters than for ground waters. At a constant degree of water closure, the temperature rise on the machine depends on:

- the energy deliberately added, eg hot water on showers and steam added to aid pulp dispersion or ink dispersion in recycled systems and
- that dissipated from electrical energy.

This energy input at the wet end is machine specific and rather difficult to predict, but can be up to about 1 GJ/tonne paper. When the energy input is constant, the temperature rise depends on the degree of water closure, but the increase can easily reach +30^{o}C in more closed water systems (see this example of increased temperature on water closure, which assumes an energy input of 0.5 GJ/tonne at the wet end and a baseline temperature of 15^{o}C and these values for several machines with fully-closed water systems).

This temperature increase may have various consequences for wet end chemistry:

- greater fibre flexibility and swelling, particularly for mechanical pulps
- increased dissolution from pulps as a result of better swelling (see this example for a chemimechanical pulp)
- increased rate of chemical reactions, which is probably undesirable in most situations as many of these are related to problems such as deposit formation.
- change in equilibrium constants such as solubility products - increased solubility would tend to lower the adsorption and hence retention of substances, but changes in the conformation of polymers may promote adsorption at increased temperature (see this example for cationic starch)
- greater rate of microbiological growth and lower oxygen solubility leading to more rapid deoxygenation and earlier onset of anaerobic conditions. The actual effect on the microbial populations is difficult to predict as it depends on the starting temperature and could decrease or increase.
- changes in the physical characteristics of materials, such as an increased softness/tackiness of some deposits leading to greater mobility and transfer of problems further down the system.
- lowered viscosity of water leading to improved water removal on the wire and in the press and drying sections and an aggravated foaming tendency.

Temporary hardness

This is the fraction of the total water hardness that is present as calcium or magnesium bicarbonate and is classed as temporary as it can be easily removed by boiling:

$$Ca(HCO_3)_2 \rightarrow CaCO_3 + H_20 + CO_2$$

It can also be removed by lime treatment:

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3 + 2H_20$$

Temporary hardness can cause precipitation problems depending on the water pH and temperature in relation to the calcium and bicarbonate (alkalinity) levels (see Langelier's equation). Conversion to permanent hardness by acid (hydrochloric or sulphuric) addition also stabilises the water in relation to possible precipitation reactions.

Tensile strength

This strength parameter is the paper's resistance to being pulled in one direction along the plane of the paper. Because of the alignment of fibres in the machine direction (MD) of the paper, the tensile strength is greater when the paper is pulled in this direction compared to the cross direction (CD). The relationship of MD to CD strength is known as the "squareness" of the sheet. There are many commercial instruments to measure tensile strength and they all involve clamping a narrow strip of paper (typically 15mm wide) between two sets of jaws and then drawing the jaws apart until the paper breaks. This test generates a curve of stress (the tensile force) against strain (the increase in length of the paper), from which a number of useful parameters can be calculated:

- ❑ the tensile strength itself, the force at the break point usually expressed as the force per unit width (N/m) or as an actual stress (force per unit area in N/m^2 or Pa) if the sheet caliper is known. The normalised tensile strength is simply the strength (N/m) divided by grammage (g/m^2) in units of N.m/g or as the breaking length (km) = tensile index (kN.m/g)/9.8. Breaking lengths of papers vary from about 2-10 km corresponding to tensile indices of about 20-100 Nm/g.
- ❑ elongation at the break point
- ❑ tensile absorption energy, which is the work to rupture the strip in J/m^2
- ❑ the modulus of elasticity (Young's Modulus), which is the slope of the initial linear part of the stress-strain curve (obeying Hook's Law) with the same units as tensile strength.

The tensile strength of individual fibres (zero-span tensile) is measured by bringing together the jaws of the tensile tester so that there is no gap. The wet tensile strength is measured simply by pre-wetting the sample. The z-direction tensile strength (internal bond strength) is measured by sticking both sides of the paper to plattens with double-sided tape and then placing this construct in the tester.

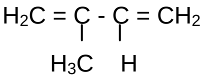
Various models have been proposed to relate the tensile strength of paper to some fundamental properties of the fibrous pulp, one of the best known being the Page equation:

$$\frac{I}{T} = \frac{9}{8Z} + \frac{3W}{L.S.B}$$

where T = tensile stress (breaking force per unit area), Z = zero-span strength, W = fibre width, L = fibre length, S = breaking stress of inter-fibre bonds and B = relative bonded area.

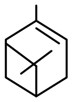
Terpenoids

These organic chemicals (sometimes still referred to, incorrectly, as terpenes) are rather complex natural chemicals that are based on the isoprene unit (see below). Their formulae can all be written in the form $(C_5H_8)_n$ and are classified into various types depending on the value of n, eg the monoterpenoids where n = 1 and the sesquiterpenoids where n = 2. Terpenoids are present in the extractives fraction of wood, two examples being α- and β-pinene (both n = 2), as shown below.

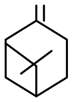


$H_2C = \underset{H_3C}{C} - \underset{H}{C} = CH_2$

Isoprene



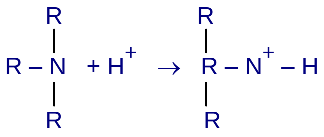
α-pinene



β-pinene

Tertiary nitrogen

Nitrogen-containing groups are incorporated in some polymers to confer a cationic charge on the polymer chain. The nitrogen is tertiary when it attached to three carbon atoms and can thus carry a positive charge only when it is protonated (as shown at right) so the charge is pH dependent.



$R - \overset{R}{\underset{R}{N}} + H^+ \rightarrow R - \overset{R}{\underset{R}{N^+}} - H$

Example of chemicals with some tertiary nitrogens are polyethyleneimine and the dendrimers based on polypropyleneimine. Other types of nitrogen are quaternary, secondary (connected to two carbon atoms) and primary (connected to three carbon atoms). The charge difference between a cationic starch with tertiary or quaternary nitrogens is illustrated here.

Test liner

This is the name for the recycled version of Kraft linerboard.

Thermally-modified starches

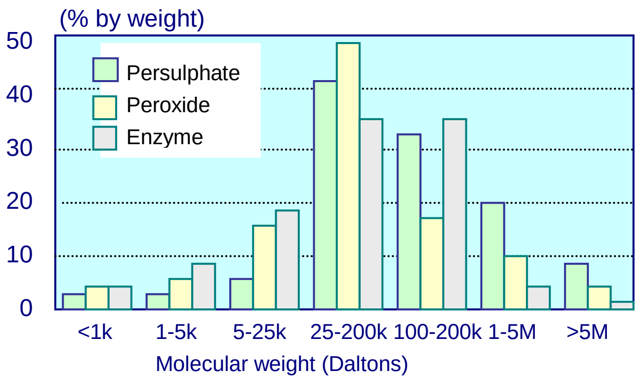
These starches are produced by the starch manufacturer by acid treatment of a native starch at high temperature, which initially depolymerises the starch into quite short fragments. These then repolymerise to give branched structures that are still much smaller than the parent molecules.

Thermo-chemical starches

These in-mill converted native starches are widely used for surface application, particularly in the manufacture of packaging grades such as recycled fluting. They are rarely, if ever, used at the wet end as they have little affinity for the particulate matrix and are thus very poorly retained. Enzyme-converted starches are an alternative type for this application.

Thermo-chemical starches are normally produced by jet cooking, in which the starch suspension is steam-heated very rapidly to about 150°C and is then held for a short time (4-5 minutes) in a contact zone in the presence of chemical oxidants. The most common chemicals are hydrogen peroxide (usually with a small amount of copper sulphate as catalyst) or ammonium persulphate at doses of 0.1-0.25% (as 100% active materials) on the starch solids. This treatment brings about some depolymerisation of the starch molecules and some (slight) oxidation of the pendant $-CH_2OH$ group to -COOH groups. These starches thus bear some similarity to oxidised starches. Addition rates at the size press are typically around 5% on the base paper, but can be higher.

The molecular weight distribution of the resulting starch solution depends on the conversion process, as showed in the picture at right. Both enzyme-converted and peroxide chemical-converted starches generate a relatively high proportion of low molecular weight starch fragments which will contribute little to the functionality of the starch in the paper. By contrast, the persulphate-oxidised starch not only produces little low molecular weight material, but also maintains a relatively high proportion of high molecular mass solids with excellent strengthening functionality.



Source: Bergh, NO "Starches" in "Surface application of paper chemicals", Chapter 4, 69-102, Blackie, 1997.

Thermodynamics

This is a very important subject within physical chemistry and is the science of the different kinds of energy and the transformations between them. The thermodynamic aspects of interactions between substances determine whether or not they are likely or possible to take place, but kinetics aspects determine whether it actually does take place within the timeframe available.

There are three well-known fundamental laws of thermodynamics:

- 1st law on energy conservation
  Energy cannot be created or destroyed, only converted from one form to another.
- 2nd law on the direction of natural processes
  The entropy of a natural system can only increase, which is usually interpreted as meaning that the degree of disorder or randomness must increase.
- 3rd law on the entropy scale
  The entropy of a pure, crystalline substance is zero at the absolute zero of temperature (0°K) and this allows the calculation of chemical equilibrium constants from thermal data.

Thermomechanical pulp (TMP)

This type of mechanical pulp is produced by a development of the original refiner mechanical pulping (RMP) process in which the wood chips are pre-steamed before refining. The first plant was installed in the late 1960s and many plants have been installed from the 1970s onwards. The equipment is very similar to that used in the RMP process, comprising either single or double disc refiners or conical refiners. Due to the nature of the mechanical action on the chips, thermo-mechanical pulps become deformed due to fibre twisting and curling (called latency), which has to be removed prior to screening. The TMP process is often modified to produce a stronger, chemically-modified pulp in the form of CTMP.

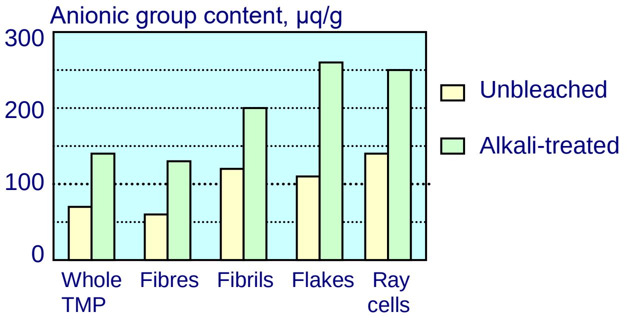
Newer TMP variants (such as the Thermopulp process) operate 2 stages of treatment, the first at a relatively low temperature and the second at a higher temperature and pressure, which gives an overall 10-20% reduction in energy use. TMPs are the strongest mechanical pulps, but have a much higher energy consumption than what is the main alternative process today, pressurised groundwood. The pulps have a lower fines content than most groundwood pulps, typically 28-30% for spruce.

In the pulping of spruce, one of the most widely-used woods for mechanical pulps, about 4% of the wood substances dissolve during the process, the largest fraction being the galactoglucomannans. Most of this material is retained in the pulping circuits through thickening of the pulp, the amount passing forward to the paper machine being dependent on the overall washing efficiency. The galactoglucomannans remaining with the pulp help to stabilise the colloidal pitch particles by a steric stabilisation mechanism, but this breaks down when the pulp is bleached. Pitch from TMP is treatable by enzymes and this also gives a simultaneous improvement in paper strength (see this example).

The most problematic substances within the pulp's dissolved organics is the sub-set of anionic materials, typical levels for spruce TMPs being about 100 μeq/g pulp. Various studies on spruce TMP have provided useful data on some of the characteristics of these charged substances:

- the surface charge was shown to be only about 10% of the total charge
- the charged substances that dissolved in the liquid phase are about 20% of the total
- the pulp fines contain higher levels of charged substances (140 μeq/g) than pulp fibres (80 μeq/g).

Further data on the distribution of total anionic substances (ie those measured by titration with Polybrene) in spruce TMP is shown in the figure at right, which confirms the higher level in fines. In this study, the fines were sub-divided further (into fibrils, flakes and ray cells) depending on their settling characteristics under different conditions. Alkali treatment simulated the alkaline conditions in peroxide bleaching (but without any peroxide present), confirming the increased anionic levels caused by hydrolysis of pectin esters.



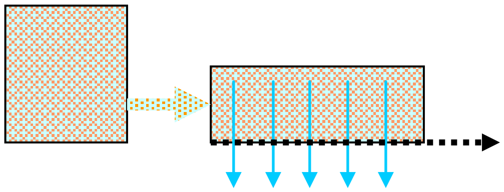
Source: Sundberg et al J.Pulp Paper Science, 2003, 29, 5, 173-177,

Comparative data for the charged substances present in one unbleached TMP is given in this table using different charge titration techniques. The variation in the cationic demand on a paper machine using a mixture of unbleached and bleached TMP is shown here. The effect of TMP dissolved solids on its drainage characteristics is shown here.

Thickening

This term has several possible meanings in papermaking:

- at the wet end of the paper machine as part of the overall process of water removal from the papermaking stock, thickening is the drainage process that follows the filtration stage once the consistency reaches the few per cent level (at about the wet line). In thickening, water removal takes place throughout the water body and the consistency remains constant throughout this depth, progressively increasing as water is removed (as shown at right). This mode of drainage gives a more uniform z-distribution than filtration.



- in coating, chemicals are used to increase the viscosity of (ie thicken) the coating mix and thus modify its rheological characteristics. Coating thickeners include alginates, CMC and starches.

- in pulping, bleaching and deinking, the pulp is usually thickened to increase its consistency. This may be done within the process simply to separate water circuits (particularly where different chemistries are used) and at the end of the process to minimise the water load passing to the paper machine or to a final drying stage. Sometimes, this process is referred to as washing where the emphasis is more on removing undesirable dissolved substances in the liquid phase rather than on simply removing water for economic reasons (eg to lower the water load on a high temperature treatment stage such as disperging within a deinking process).

Thiosulphate

This ion ($S_2O_3^{2-}$) can be found in papermaking systems following the use of sodium hydrosulphite for bleaching as this chemical can decompose into a mixture of thiosulphate and sulphite. Concentrations of a few 10s mg/l have been quoted for newsprint machines using hydrosulphite bleached mechanical pulps. Its presence at the wet end is deleterious due to its contribution to corrosive activity.

Thixotropic

This is an important rheological property of some substances or systems and means that their viscosity declines with shearing time.

Tinctorial value

This term is used in colour chemistry to indicate the strength of coloration produced per unit mass of colorant. Dyes are better in this respect than coloured pigments.

Tissues

These are an important set of paper products that are normally placed in the same category as towels, the two together comprising about 7% of global paper production. The main tissue grades are toilet tissue and facial tissue, the main difference being that the latter has a degree of wet strength, but not as much as in towel products. Other grades that are also referred to as tissue are certain soft wrapping papers and cigarette tissue.

The composition of tissue products is dominated by the pulp component, which ranges from 100% bleached chemical (Kraft) pulp to 100% deinked pulp. The latter inevitably contains some residual filler, but this is kept as low as practicable (few per cent). Fresh filler would, of course never be added to these grades. In most cases, the pulp accounts for at least 99% of the tissue dry weight, the remainder being a mixture of the following:

- dry strength chemicals, both starch and polyacrylamide types being used to compensate for the normal absence of any pulp refining due to its adverse effect on softness and bulk
- wet strength chemicals (facial tissue only), predominantly of the polyamide-epichlorhydrin type
- softening or debonding agents (not always used)
- fluorescent brightener which are possibly, but not commonly, used on white grades
- dyes on coloured grades.

The normal range of process control chemicals may be used depending on machine conditions, although it is not uncommon for retention aids not to be used due to the adverse effect of fines (particularly any filler fines from use of deinked pulp) on tissue softness. One set of chemical additives unique to tissue and towel machines are the chemicals sprayed onto the drying cylinder or sometimes added at the wet end to enhance creping.

Titanium dioxide

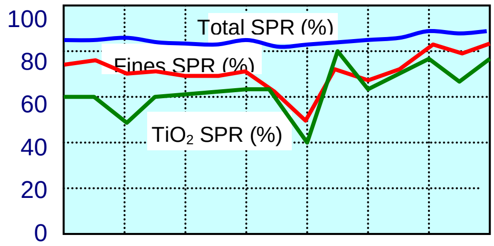
Titanium dioxide (TiO_2) is the supreme opacifying pigment, but is used sparingly because of its very high cost (more then bleached chemical wood pulp). It accounts for a small proportion of total filler/pigment use (about 2% globally) with half of this being in North America. Its main use is in lightweight printing papers, where good opacity is essential, but where little strength loss can be tolerated due to the low grammage. In these grades, TiO_2 is used at levels of no more than about 5%, but it is also used at very high levels (up to 40%) in resin-impregnated decorative laminate papers.

Titanium dioxide occurs in two crystalline forms – anatase in the mixed iron/titanium oxide Ilmenite and rutile in the much purer ore of the same name. There are two manufacturing processes based on either sulphuric acid (sulphate process) or chlorine gas (chloride process), the latter being mainly applied to the rutile grade. In both processes, the impurities (notably iron compounds) are dissolved and the pure titanium dioxide produced by drying at either 250^{o}C (anatase) or 900^{o}C (rutile). Both forms are used in papermaking and can be supplied in powder or slurry form (solids content 70-80%).

The difference between the rutile and anatase forms is rather subtle as, in both forms, each titanium atom is surrounded by six oxygen atoms in an octahedral arrangement and each oxygen atom is surrounded by three titanium atoms. In the rutile structure, the octahedra are turned through 90° with a twist of 45° from one layer to the next, whilst they retain their orientation in anatase. The atoms are more closely packed in rutile, which accounts for its slightly greater refractive index (2.7 compared to 2.55 for anatase) and its slightly higher density (4-4.2 kg/dm^3 compared to 3.7-3.8 kg/dm^3 for anatase). Both forms have a high whiteness, but the light absorption spectrum of rutile extends from the ultra-violet region into the blue end of visible spectrum giving it a slightly yellower tone. Titanium dioxide is the only opacifying mineral that absorbs strongly in the ultra-violet region of the spectrum, thus impairing the performance of fluorescent brighteners. Anatase absorbs less UV light than rutile and is thus preferable for wet end use when fluorescent brighteners are also used.

The surface chemistry of both types of TiO_2 is influenced by the incorporation of other oxides (silicon, alumina) onto its surface in some grades and the use of dispersants when it is supplied in a slurry form. Titanium dioxide itself has some amphoteric properties so its surface charge depends on pH, as shown in the figure here. In this particular example, the anatase had been surface treated with phosphate, removal of which shifts the charge-pH profile to match that of the rutile form. Coating the surface with silica has the same effect, whereas alumina coating increases the iso-electric point to a similar pH as for pure alumina.

The data at right is taken from a small paper machine making AKD-sized wood-free paper where the grammage was 55-60 g/m^2 except for the short period just over halfway through the sampling period when it was somewhat lower (where the retentions declined). The overall single pass retention (SPR) of the mineral fraction (predominantly clay, but including the TiO_2 component) is not shown, but was very similar to the fines SPR. The retention aid system was a combination of cationic starch and anionic polyacrylamide, which gave excellent aggregation of the filler and fibre fines although the machine speed was only 200 m/minute with consequent low shear levels. The retained ash in the paper was about 23% with total TiO_2 retentions of around 95%. This data is from the same paper machine as the second example indicating the influence of grammage on single pass retentions, which is shown here.



TMP

This is an abbreviation for thermomechanical pulp or pulping process.

TOC

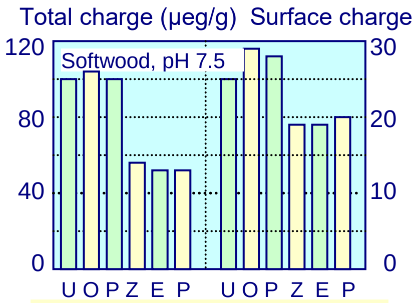
This is an abbreviation for total organic carbon, but this is discussed under dissolved organic carbon.

Totally-chlorine free (TCF) pulps

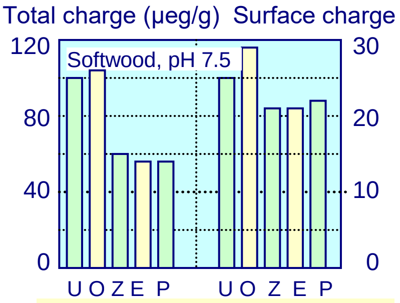
These bleached chemical pulps are produced without the use of chlorine gas, sodium hypochlorite or chlorine dioxide. Sometimes, this term is applied to bleached mechanical pulps, but this is superfluous as such pulps have never been bleached with chlorine-containing chemicals. The term TCF is also applied sometimes to bleached deinked pulps and this is more legitimate as some deinked pulps had been bleached with chlorine-containing chemicals, notably with sodium hypochlorite. TCF bleaching sequences are applied mainly to Kraft pulps, but this is simply due to the predominance of this pulp and TCF bleaching is in fact equally applicable to sulphite pulps.

TCF pulps have become quite an important pulp type since the early 1990s, but their production is quite small compared to ECF pulps. The development of TCF (and ECF) pulps has been driven by the environmental problems associated with chlorine bleaching, notably the generation of chlorinated organic by-products such as chlorinated phenols (eg pentachlorophenol), dioxins and chloroform. Although TCF pulps tend to be lumped together as single category, there may be quite important differences between different types of TCF pulp as discussed further below.

The profile of charged substances through two different TCF bleaching sequence for a softwood pulp is shown in the two figures at right and below. With one notable difference, the general level of charges across both sequences is comparable with the level across the ECF sequence shown here. The notable difference is the poor removal of charged substances during the first hydrogen peroxide (P) stage in the OPZEP sequence, but this has little impact on the level of anionic charges in the final pulp due to the efficacy of the ozone stage. However, when there are only oxygen and peroxide bleaching stages (as shown in this table), the final pulp does have a higher content of anionic substances. It has been shown that this is due to the inability of peroxide to remove the hexenuronic acids in the pulp. For both types of TCF pulp, the surface charge (that accessible to a high molecular mass polydadmac) is about 40% of the total charge. This is a much higher proportion than in the unbleached pulp (about 25%), suggesting that TCF bleaching (like ECF) selectively removes more of the charged substances within the pulp's internal structure. The effect of pH on the titratable total charge of the above OZEP-bleached pulp is shown here.



Source: Laine, J in Paperi ja Puu, 1997, 79, 8, 551-559.

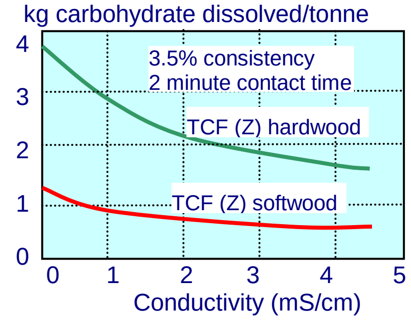


Source: Laine, J in Paperi ja Puu, 1997, 79, 8, 551-559.

Further data on the charge of TCF pulps (see this table) indicates a somewhat higher total charge (60-100 µeq/g depending on titration technique) in a hardwood (birch) TCF pulp.

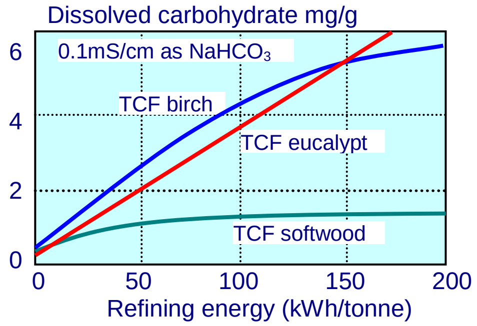
In the early days of TCF bleaching, the pulps seemed to have a higher content of potentially-soluble material than ECF pulps, but this was probably at least in part due to their relatively low brightness and incomplete removal of lignin compounds. Nevertheless, dissolution on the paper machine is still an important issue for the cleaner TCF pulps produced today.

This has been investigated in a recent study using a laboratory-bleached hardwood (birch) Kraft pulp. The results indicate that dissolution of hemi-celluloses in a laboratory disintegrator was complete after no more than about 30 minutes and dissolution increased with disintegration consistency from about 5 kg carbohydrate/tonne at 0.5% pulp to 7.5 kg/tonne at 3.5% pulp. This increased dissolution is probably due to the greater inter-fibre contact at higher consistency. These results are obtained from disintegration in a water with a low electrolyte content (100 mg/l as $NaHCO_3$), but dissolution decreases at higher electrolyte levels as shown in the figure at right. In this study, the hardwood pulp contained about 100 µeq/g anionic substances compared to about 50 µeq/g for the softwood pulp. Dissolution increases with the content of anionic substances in the pulp due to their affect on fibre swelling, but electrolytes suppress dissolution due to their inhibition of fibre swelling.

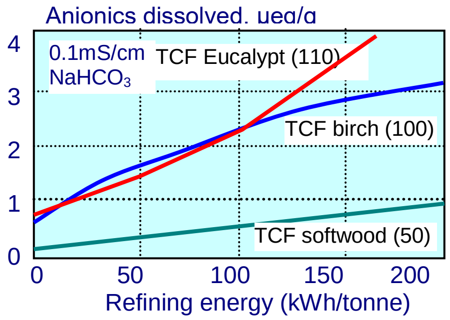


Reference: Sjostrom et al Nordic Pulp Paper Research J. 2000. 15. 5. 469-475.

When pulps are refined after slushing, further dissolution takes place as the fibrous structure is opened up by mechanical action. At low levels of electrolytes in the water, there is significant additional dissolution above that from simple slushing (see figure at right), the levels from hardwoods again being much greater than from softwoods. Increased electrolyte levels again reduce dissolution due to their adverse effect on fibre swelling (see this example in relation to the pulp's content of charged substances). Within the dissolved carbohydrate fraction there are anionic hemi-celluloses, which, when dissolved, become part of the anionic trash.



Source: Sjostrom in Nordic Pulp Paper Research J, 2000, 15, 5, 469-475.



Source: Sjostrom in Nordic Pulp Paper Research J. 2000. 15. 5. 469-475.

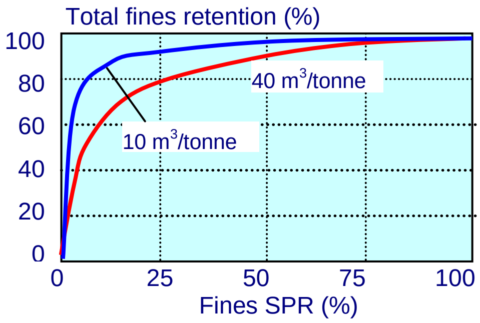
This is illustrated at left for the same pulps as in the above figure, where the number in brackets after the pulp is its total charge content in µeq/g. The charge density of the dissolved materials is about 0.5 meq/g, which is about the expected level for the glucuronoxylan hemi-celluloses. Dissolution of charged organics follows the same pattern as for carbohydrate, but it is evident that only a small fraction (<5%) of the anionic substances dissolve during refining. This is desirable for all pulps, but particularly for all bleached chemical pulps because of their relatively low content of anionic substances after bleaching. The fact that nearly all the anionic charge remains on the pulp means that the pulp retains its full ability to adsorb wet end cationic additives.

Total retention

This is the retention of the overall papermaking system and is the mass of material retained in the paper compared to the amount entering the system (see retention for comparison with meaning of single pass retention, SPR). It is thus a measure of the total system efficiency in converting raw materials into product and is sometimes referred to as the process yield. The best way to understand this term and its relationship with other key variables is through use of the model of the papermaking system. Using this, the following simplified relationship can be developed for a simple papermaking circuit with no saveall:

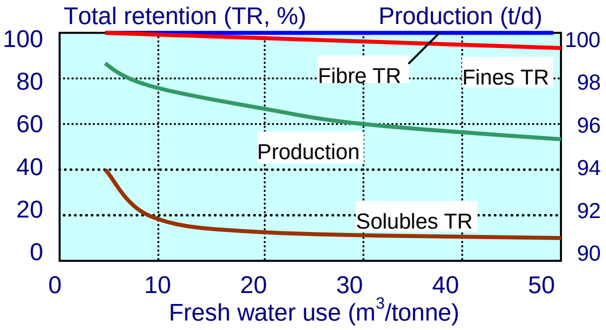
Total retention = SPR/[1-X(1-SPR)] where X = degree of closure of water circuit

The degree of closure can be defined in different ways such as the % recycling of whitewater, but, in the examples below, this will be converted into a specific water flow (m^3/tonne paper). In using this simple equation, the SPR for particulates can only take an assumed value, whereas the SPR of dissolved solids can either be calculated from the water balance or be given a realistic value (ie in the range 0.2 to 2%). It should be emphasised that the fresh water consumption used in this model is that entering the main papermaking circuit only, ie on sprays (flowbox, wire) and for backwater make-up. It does not include fresh water used on separate circuits such as vacuum pump sealing or cooling.



The single pass retention of particulate solids is influenced by many factors, but, for a given set of conditions, it is manipulated by the addition of retention aids. It is evident from the figure at right, that the total retention rises with increased single pass retention, but the rate of improvement slows down at high SPR values. It is also evident that increasing the SPR has the greatest value in improving total retention on machines where this is otherwise at its lowest, ie on machines with open water systems. The effect of the change in fines SPR on flowbox consistency is shown here.

The single pass retention of dissolved solids cannot be manipulated in this way and it is clear from the above figure that, with SPRs around 1%, their total retention is low, but increases substantially on closing up. This impact of water closure in the main papermaking circuit is shown in more detail in the figure at left. The reason for the increased total retention on water closure is that, although the amount of water entering the drying section remains constant, the concentration of dissolved solids in that water increases. The calculation in this figure is based on a level of 20 kg dissolved solids entering the system per tonne pulp used.



The same pattern of improved total retention on closure also holds true for the particulate solids, but the increase is much less dramatic. This model assumes that the SPR of the fines fraction remains constant (at 50%) on closing up, but this may not be the case. For example, the build-up in the concentration of the anionic trash fraction of the dissolved solids may adversely affect the efficiency of retention aids and, unless the retention aid dose was increased, the fines SPR would decrease. This would partially negate the improvement in total retention illustrated above. Because the fibre fraction has a high SPR (95% assumed in the above figure), its total retention is always very high, even in an open water system.

The combined effect of better retention of fines and dissolved solids gives a 2-3% lift in total production, but this would only be achieved in practice if the machine can maintain the same runnability in a closed water system as in an open system. One of the risks in operating paper machines with substantially closed water systems is that the theoretical benefits illustrated above are sometimes negated by poor runnability (and possible impaired paper quality) caused by the many problems that can occur in closed systems (see this list). These potential problems are driven by the increased circuit concentrations and temperature and these wider impacts of water closure in terms of wet end chemistry are discussed under that heading.

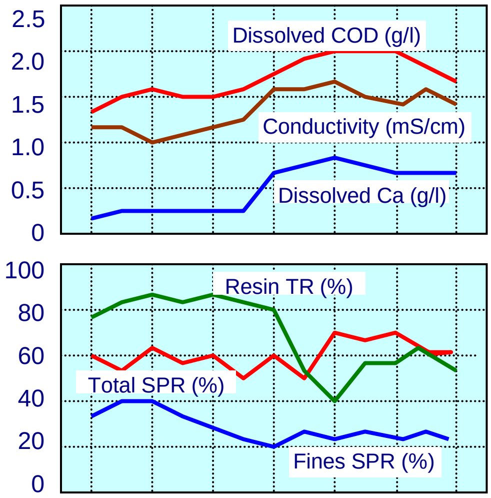
Towels

These are an important set of paper products that are normally classified along with tissues, the two together comprising about 7% of global paper production. The pulp component dominates towel composition, but, compared to tissue grades, recycled pulps tend to be used more over virgin chemical pulps. As with tissues, the pulp accounts for at least 99% of the tissue dry weight, the remainder being a mixture of the following:

- dry strength chemicals, both starch and polyacrylamide types
- wet strength chemicals, predominantly of the polyamide-epichlorhydrin type
- softening/debonding agents (less used than for tissue)
- dyes on coloured grades.

The normal range of process control chemicals may be used depending on machine conditions, the use of retention aids being more common than on tissue grades due to the lower requirement for softness and therefore greater tolerance of fibre fines/ash. One set of chemical additives unique to tissue and towel machines are the chemicals sprayed onto the drying cylinder (where present) or sometimes added at the wet end to enhance creping.

Today, towelling grades are made principally with PAE resins, but UF resins may still be used because of their relative cheapness. The following example illustrates some of the wet end chemistry issues involved in recycled towel manufacture with UF resins. The machine makes 50 g/m^2 towel from non-deinked pre-consumer recovered papers with two different grades in use. The machine uses alum/sulphuric acid to lower the wet end pH (to about 4), the level of alum/acid addition being dependent largely on the pulp's calcium carbonate content. The two figures illustrate the change in system parameters over the course of four days during which the machine changed from one recycled pulp to the other. From the first figure, it is clear that the second pulp contained more calcium carbonate than the first (raising the level of dissolved calcium, sulphate [not shown] and hence the overall conductivity) and of dissolved organics (COD). The second figure shows the change in various retention parameters with the same retention agent (cationic polyacrylamide) in use



on both grades. The fines single pass retention (SPR) does appear to decrease somewhat, but the average SPR of the total furnish does not change appreciably between the two furnishes (the fines content of the second furnish being lower due to calcium carbonate dissolution). The SPR of the adsorbed UF resin (not shown) is very similar to that of the particulate fines, but the total resin retention is halved on the second furnish. The reason for the decline in total resin retention is its impaired adsorption, which is caused by the higher concentration of dissolved calcium and possibly also by the higher dissolved organics (and its anionic trash component). A similar effect of dissolved calcium on the adsorption of a PAE resin in laboratory experiments is shown here.

Tracheid

These are long (up to 4mm) tapering cells with a pitted surface that run longitudinally along the trunk in softwoods, but are absent from hardwoods. They are more commonly referred to as fibres even though the term "fibre" should be reserved just for the dominant cell type present in hardwoods.

Turbidity

This is an empirical measurement of fine colloidal particles, which is measured by observing the light scattered at 90^o to the incident light. It has widely been used in the environmental field as an indicator of water quality. In papermaking, it is mainly applied to whitewaters from paper machines or filtrates from laboratory studies and can be measured by many on-line consistency sensors. The most common turbidity scale is formazin turbidity units (FTU).

Two-sidedness

This term refers to the tendency of some papers to have a non-uniform distribution of materials in the z-direction of the paper (see example for filler distribution here). It is caused by the fact that finer particulate solids are retained by a purely filtration or straining mechanism through the consolidating paper web. This means that the top side of the paper will tend to have a higher proportion of such solids and this may affect certain functional characteristics of the product. For example, the paper may be smoother on the top-side than on the wire-side due a higher filler content. Some materials with an initially non-uniform z-distribution are able to re-distribute themselves more uniformly through their ability to melt in the drying section, the best examples of this being wet end sizes. The most searching examination of the two-sidedness is the evenness of coloration for dyed papers as any unevenness is readily apparent by simple visual examination. Other examples of two sidedness are in terms of fibre orientation, which is influenced by the efflux ratio and the physical appearance of the two surfaces, which may be influenced by marking from wire and press fabrics.

On any paper machine, two-sidedness can be best minimised by ensuring that the finer particulate solids are hetero-flocculated with the larger fibrous solids, a process which is conducted in order to improve their single pass retention and the overall drainage characteristics of the stock. This two-sidedness effect is also minimised by the newer types of former such as gap formers and is eliminated inherently in the products from duplex machines, which have two quite separate formers. A duplex machine as defined above is not simply a normal 2-ply product (which brings together the wire and top sides), but a machine where similar faces (top-top or wire-wire) are brought together before pressing and drying.

UBK

This abbreviation is used for unbleached Kraft.

UF resin

This is an abbreviation for urea-formaldehyde resins.

Unbleached chemical pulps

This is the smaller of the two types of chemical pulp and is itself divided into two main sub-categories:

- unbleached Kraft pulp, largely for linerboard
- neutral sulphite semi-chemical pulp for fluting/corrugating medium.

The production of unbleached sulphite pulps is small due to their declining production, despite their useful characteristic of having a relatively high brightness for an unbleached pulp.

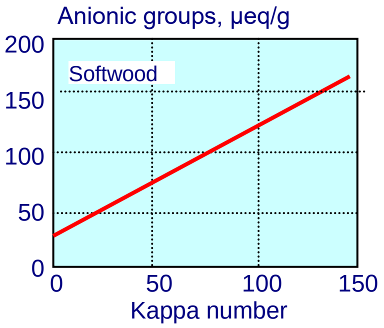
Unbleached Kraft pulps

This type of Kraft pulp is used largely for the manufacture of linerboard, although this grade can also be made from 100% recycled pulps or a blend of unbleached Kraft and recycled pulps. Unbleached Kraft pulp for linerboard is made at integrated sites, but some unbleached Kraft market pulp is made for grades such as bag papers. The latter are cooked to a slightly lower Kappa number (40-60) than for linerboard pulps (60-120), the residual lignin giving an ISO brightness of 15-30. As linerboard is often made as a duplex product (with a secondary flowbox), two different grades of unbleached Kraft pulp are used for linerboard - a cleaner, lower yield pulp for the top (printing) surface with a higher yield, darker pulp underneath. Unbleached Kraft pulps are predominantly made from softwoods such as pine.

The key papermaking qualities of unbleached Kraft pulps are:

- strength, particularly stiffness as well as normal tensile. This is determined by a combination of the pulp's physical properties (ie particle size distribution in terms of fibre length and fines content) and the residual lignin content, which is usually well-controlled via the Kappa Number as this determines the extent of Kraft cooking.
- productivity as influenced by the pulp's water removal characteristics (see examples under pressing and drying sections)
- response to wet end sizing chemicals as linerboard is always sized (see this example for AKD)
- runnability in the sense of containing the minimum level of substances that can cause problems on the paper machine, notably pitch and anionic trash in the case of unbleached Kraft pulps.

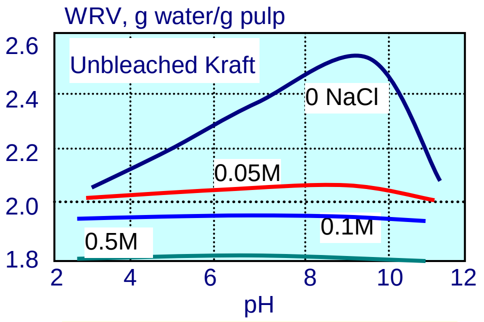
Most of the non-cellulosic material in unbleached Kraft pulps is hemi-cellulose (20-30% of total) with a much lower level of lignin (4-7% of total) - the level of both substances (for a particular wood type and yield) depend critically on the efficiency of pulp washing. The alkaline cooking conditions in the Kraft process should ensure that the pitch content of the unbleached Kraft pulps is reasonably low, but wood-derived calcium tends to keep at least some of the fatty/resin acids with the pulp. Due to the hydrolysis and saponification of wood extractives, the relatively small amount left in the pulp is usually ionised under papermaking conditions and there is thus potential for further deposition reactions with calcium ions on the paper machine. From this example, it would also seem that the anionic groups within the fibre wall of unbleached Kraft pulps would also be associated with calcium ions.



Source: Lindstrom, Nordic Pulp and Paper J., 1992, 4, 181-192

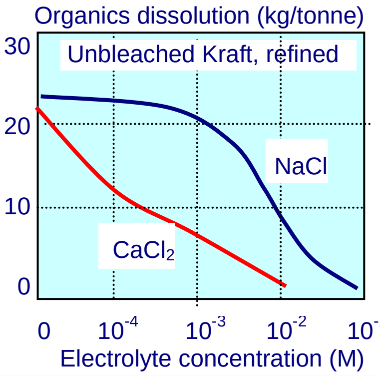
In addition to pitch, the main issues for unbleached Kraft pulps in relation to wet end chemistry are the residual lignins and hemi-celluloses that have some anionic charge character and are thus able to exert a cationic demand. Although the charge character of Kraft pulps is less dependent on the lignin content than is the case for sulphite pulps, the Kappa number of an unbleached Kraft pulp is still a reasonable indicator of its charge content (as shown at right for a softwood pulp). Other studies have quoted comparable values for other unbleached Kraft pulps, ie 50-150 µeq/g over the normal Kappa range (also see comparative data in this table using different charge titration techniques).

The relative charge contribution of the hemi-cellulose carboxyls (pK = 3.4) and lignin carboxyls (pK = 5.5) in unbleached Kraft has been determined as about 4:1 over a range of lignin contents with the total charge covering a similar range to the above figures. The relationship between surface charge (zeta potential) and the content of anionic groups in some unbleached Kraft pulps is shown here. The effect of pH on the titratable charge of an unbleached softwood Kraft pulp is shown here, again indicating a charge of about 100 µeq/g at normal papermaking pH levels (6-8). The adverse effect of Kraft lignin on the performance of cationic polymers is shown here for polyethyleneimine.



Source: Lindstrom, Nordic Pulp Paper Research J., 1992, 4, 181-192.

The swelling of pulps is important in relation to paper strength and is also affected by the pulp's charge content. As shown at right, the swelling of unbleached Kraft pulp occurs at higher pH than in sulphite pulps due to the presence of acidic groups with higher pK values. As with other pulps, increased electrolyte levels restrict swelling such that, in most papermaking systems, pH would have little influence on it. Due to their relatively high content of charged substances, unbleached Kraft pulps swell more than unbleached sulphite pulps and bleached Kraft pulps. The nature of the cations associated with the anionic groups is also important and these can change depending on the cation balance in the bulk solution (see examples under ion exchange and Donnan effect).

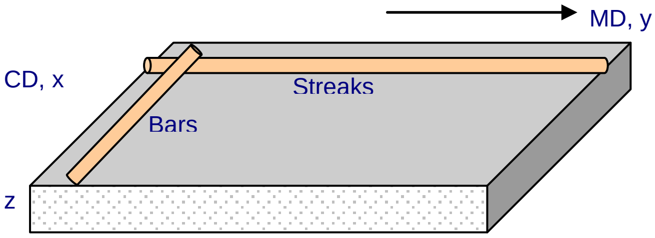


Reference:.Lindstrom in Nordic Pulp Paper Research J., 1992, 4, 181-192.

When the charged organic substances remain associated with the fibre wall, they are valuable for increasing pulp swelling and as adsorption points for cationic additives. However, the swelling also allows organic substances (both charged and uncharged) to diffuse through the fibre wall into the bulk solution (which is undesirable). Due to this dependence on the degree of swelling, the release of dissolved organics also depends on the electrolyte content of the water, as shown in the figure to the left. The greater deswelling effect of divalent cations compared to monovalent cations has a dramatic effect, which would severely curtail dissolution in real papermaking systems.

Uniformity

This term is discussed here in relation to the uniformity of paper products, which is an important quality issue. Paper is a complex 3-dimensional structure, which always exhibits some within-reel variability due to the physical and chemical heterogeneity of its raw materials. The terminology of paper uniformity (or usually the lack of it) can be confusing in terms of its directionality as a variability in the cross-direction (ie the paper is different in some way at different positions across its width) is actually aligned in the machine direction.



The nature of this variability and its causes depend on the paper axis:

- ❑ cross (x) - direction (CD) uniformity (eg poor uniformity due to streaking) is little influenced by the chemistry of the papermaking stock, but has more to do with the engineering of the approach flow system and the sophistication of the flowbox outlet (slice) controls. Striations (usually micro-striations) are another sort of MD-aligned variability, but this is caused by differential shrinkage during drying that originates from sheet variability in the z-direction.
- ❑ machine (y) - direction (MD) uniformity (eg poor uniformity due to barring) is influenced by the uniformity of the thin stock and the variability in the single pass retention of its components, which is affected by many aspects of wet end chemistry (see these examples of the influence of the level of fines SPR on the variability of fines SPR). There may also be purely mechanical explanations for such variability such as inconsistency in the thick stock supply.
- ❑ wire (z) - direction uniformity (eg two-sidedness and fibre tilt) is influenced strongly by the drainage and consolidation processes, which are in turn influenced strongly by the stock composition and its state of aggregation (see this example of the influence of filler SPR on filler z-distribution). Such differences between the two sides can lead to obvious functionality problems (eg differential sizing) and difficulties related to curl.

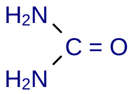
The areal (xy) - uniformity of paper can be analysed at two levels:

- ❑ its macro-uniformity, such as:
  - the streaking and barring problems mentioned above
  - general blotchiness or mottle
  - presence/absence of holes, which are affected by, for example, entrained gases
  - presence of disfiguring materials like spots or agglomerations of slime, pitch and stickies.
- ❑ its micro-uniformity or "formation" quality, which, like the z-distribution, is affected by the state of aggregation of the total particulate components, including genuine fibres (macro-flocculation) as well as fines. However, whilst a high fines single pass retention improves z-direction uniformity, it has the opposite effect on xy-direction uniformity, this being one of the dangers in trying to achieve a very high (too high) fines SPR.

Clearly therefore, the chemistry of the system has a major influence on the overall uniformity of paper products and additives such as retention aids need careful optimisation in order to maximise fines single pass retention and sheet structure.

Urea

This chemical (formula at right) occurs in two different forms in the papermaking process. It is present as a solubiliser in some dye/brightener formulations and it forms one of the two building blocks for the urea-formaldehyde resins that are used to provide wet strength and the urea-formaldehyde pigments for improving paper opacity. Urea also used to be present in some rosin sizes and is formed when FAS bleach is used for decolorisation of deinked pulps and machine broke. When present as free urea, it is easily hydrolysed to ammonia by the urease enzyme.



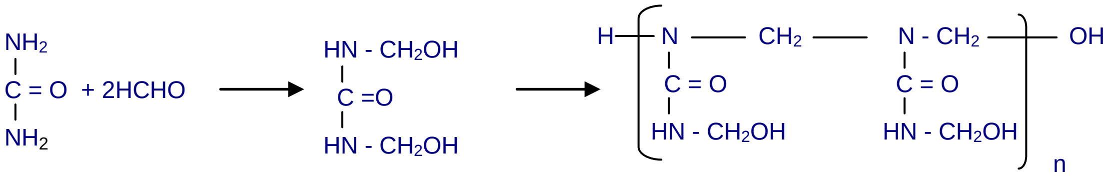
Urea-formaldehyde pigments

These pigments have the same chemistry as the wet strength UF resins, but the product is in the form of a fine particle size dispersion as the reaction between urea and formaldehyde has been allowed to go to completion to form the insoluble fully cross-linked product. These pigments have applications similar to mineral fillers, but being organic, they do not contribute to the paper's ash content and, being much lighter than mineral fillers (material density about 1.5 g/cm^3), they have a lesser impact on paper density. They are made of very small primary particles (100-200 nm) which produce aggregates of 3-6 μm diameter. The high light-scattering coefficient (about 450 m^2/kg) is due to a combination of small particle size and a refractive index (about 1.6) slightly higher than most mineral fillers. Like other synthetic pigments, they also have a very high brightness (> 95% ISO). They are usually supplied as high solids content suspensions (60-80% by weight). Because of their excellent opacifying characteristics, they are often used as titanium dioxide extenders.

Urea-formaldehyde (UF) resins

UF resins are used as wet strength agents and are made from urea and formaldehyde (see figure below). These two chemicals initially react under neutral/slightly alkaline conditions to form dimethylolurea, which is known as the A-stage resin. Under acid conditions and high temperature, this material condenses to yield a series of polymers of decreasing water solubility as hydroxyl groups are eliminated (B-stage resin). The solubility is improved by the addition of sulphite to form sulphonated resins, which are anionic in character and thus not well-adsorbed on fibre unless alum is added. Cationic resins are made by the addition of polyfunctional amines such as ethylenediamine and diethylenetriamine and these are the most common type of UF resin used in papermaking.

The normal papermaking resin is the B-stage resin, which then reacts further in the drying section through further condensation reactions between the hydroxyls in the methylol groups and nitrogen-bound hydrogens, generating the linking methylene group (- CH_2 -). This forms the 3-dimensional cross-linked C-stage resin, which physically protects the fibre from water penetration. It is not thought that UF resins react significantly with cellulose, which is consistent with their negligible effect on dry strength.



The formation of the C-stage polymer takes place at the elevated temperatures in the drying section of the paper machine, but this also requires acidic conditions. Above pH 5, this reaction is quite slow so the wet end usually has to be operated at pH 4-4.5 (sometimes as low as 3.5) in order to ensure adequate acidity within the drying section. This low pH promotes corrosion and also tends to lower the negative charge on pulps, thus reducing the driving force for adsorption of cationic substances. Even with this low pH, the contact time at a high-enough temperature within the drying section is not usually adequate to cure fully the UF resin, so the product has to be allowed to cure further during storage, albeit very slowly at ambient temperatures (up to 4 weeks).

Commercial UF resins contain 25-50% solids and have a neutral pH (to prevent further condensation reactions which would lead to gelation and ultimate insolubility). Because of the ongoing chemical activity, even at neutral pH, shelf-life is limited to no more than 6 months depending on ambient temperatures. UF resins are usually added at the end of the thick stock system in order to maximise adsorption on the particulate matrix, but are pre-diluted to facilitate mixing and distribution in the stock. In the case of cationic resins, the low pH is best controlled by the addition of sulphuric acid and not alum as this would tend to reduce resin adsorption and also unnecessarily complicates wet end chemistry. The overall performance of UF resins is influenced by a number of factors related to its initial adsorption step (pulp charge, the presence of other species competing for adsorption sites, the presence of anionic trash, etc) and then on its final curing efficiency. An example of some chemistry effects on UF resin retention is shown here for towel machine. Even under ideal conditions, UF resins are not as effective on a weight basis as MF and PAE resins, but they are the cheapest form of wet strength resin and it is possible to achieve wet/dry strengths of about 35% at a maximum dose of about 2% resin solids on product.

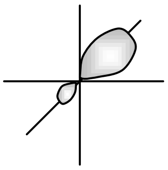
UF resins can contain up to 6% free formaldehyde, but this can be reduced to 1-2% by different techniques without unacceptable loss of performance. The free formaldehyde level in a UF resin is an equilibrium concentration for each grade that tends to re-establish itself whatever the free formaldehyde level at the time of packing. Unlike the resin itself, the free formaldehyde is not adsorbed by the particulate solids and builds up in the water system to a level dictated by the machine's degree of water closure. All storage vessels should thus be covered or enclosed, but, even then, the equilibrium levels in the water system can cause odour, which is normally controlled by ensuring adequate machine house ventilation. Formaldehyde is also emitted during paper drying from the free aldehyde retained through its presence in the water carried into the dryers and from formaldehyde released from curing reactions.

Broke from UF resin wet strengthened paper should be repulped as soon as possible after the reel-up in view of the continuing cure reaction which impairs repulpability. Repulping is normally carried out at slightly acid conditions (pH 3-4) and at raised temperatures (60-80^{o}C). The contact time is determined by the degree of cure, but is usually less than 1 hour. Formaldehyde is again released during repulping, so the pulper should be covered and the exhaust gas dealt with appropriately.

Valency

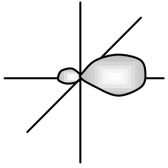
The bonding ability of elements is determined by the number of valency electrons, which are the unpaired electrons in the outermost orbital. The shape of orbitals is discussed for the various groups in the Periodic Table under electrons. The valency of some elements is not what might be expected at first glance due to the tendency for hybridisation (mixing) of orbitals. For example, the electrons in carbon are designated $1s^2$, $2s^2$, $2p^2$ so carbon might thus be expected to have a valency of 2 as there are two unpaired electrons in the 2p orbital. However, the 2s and 2p orbitals are in fact hybridised (mixed) to form an sp^3 hybrid with four unpaired electrons so carbon has a valency of four. The shape of the sp^3 orbitals (see representation at right) gives rise to the symmetrical tetrahedral structure for simple carbon compounds like methane, CH_4, where each hydrogen atom is at the corner of the tetrahedron. Each linear bond formed between carbon and the hydrogens (called a σ [sigma)] bond) arises from the overlapping of one sp^3 orbital and the 1s orbital of each hydrogen.

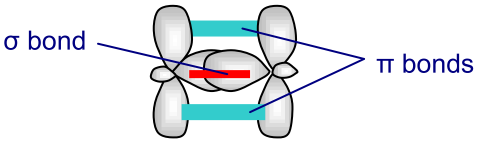
sp^3 hybrid



The orbitals in carbon can be hybridised in two other ways when it forms double bonds (as in ethylene, $H_2C = CH_2$) using sp^2 hybrid orbitals and triple bonds (as in acetylene, $HC \equiv CH$) using sp hybrids. Taking the case of ethylene, each sp^2 orbital is directed along one of the major axes (as shown at right) and part of the double bond (its linear σ bond) arises from overlapping of one of the sp^2 orbitals on each carbon atom. However, the p orbital in the z-axis has not been hybridised and these two orbitals on each carbon atom can overlap on either side of the x-axis to give a second bond (known as a π [pi] bond). A representation of the double bond is shown in the diagram at right.

sp^2 hybrid along x-axis





The double bonds from sp^2 hybridised carbon are slightly shorter than single C - C bonds and, as the three bonds are all in one plane, this is known as a trigonal planar conformation. No rotation is possible about the double bond and this explains the two forms (cis and trans) of some compounds with double bonds (see isomers). The carbon atoms in benzene are also connected by sp^2-hybridised carbons, but, whereas the electrons in the π-bond in ethylene are localised between the two carbon atoms, the π-bonding electrons in benzene are delocalised across all 6 carbon atoms as this represents the lowest energy configuration. This type of alternating single and double bond structure is referred to as conjugation and is very important in dye chemistry.

Hybridisation of bonding orbitals is also important for the covalent compounds formed by nitrogen and oxygen. For example, oxygen has an electronic structure of $1s^2$, $2s^2$, $2p_x^{2}$, $2p_y$, $2p_z$ so has a formal valency of 2. However, it is known that the water molecule has an approximately tetrahedral structure with the four tetrahedral positions being occupied by two sets of paired electrons and two hydrogen atoms. This is explained by sp^3 hybridisation of the 2s and 2p orbitals. In the hydrated proton (the hydroxonium ion, H_3O^+), the oxygen cation (O^+) has a formal valency of three with only one set of paired electrons. This is still formed by sp^3 hybridisation of the 2s and 2p orbitals, but the structure is more of a trigonal pyramid than a tetrahedron.

Electrons in the d orbitals can also be utilised to form more complex hybrid orbitals, but these only come into play for elements in the second row and above of the Periodic Table. Hybrid orbitals such as d^2sp^3 are particularly important in the chemistry of the transition metals.

Van der Waals forces

These natural forces of attraction exist between all substances and result from interactions between various dipoles (intra-molecular charge separation) that are present to varying degrees in many materials. There are three different types of attractive force:

- orientation (Keesom) forces between permanent dipoles
- induction (Debye) forces between permanent and induced dipoles
- dispersion (London) forces between oscillating induced dipoles, which depend on the substance's polarisability; these are the most significant forces for all except very polar substances.

These forces play a key role in the cohesive forces between materials (eg in gases becoming liquids) and they also contribute to the mechanism of surface tension. Such forces are much weaker than those involved in chemical bonding, but are comparable to the strength of hydrogen bonds. Although the attractive force decays very rapidly with separation distance for individual molecules, the summation of the forces between all molecules within a particle makes the overall force very significant in terms of particle aggregation. Estimation of the force depends on the model used for the surfaces, eg flat plates or spheres. An approximate expression for the force between identical spheres, valid for separations up to about 20 nm, is as follows:

van der Waals attractive force, $V_A = -A.d /12H$
where d = particle radius, H = inter-particle distance
and A = Hamaker "constant" which depends on the material's density and polarisability.

The van der Waals attractive force plays an important role in determining the net force between particles and hence in the degree of particle aggregation.

Vegetable parchment

This is a type of paper made by passing the base paper through a bath of sulphuric acid, which gelatinises the cellulose on the sheet surface and re-deposits it in the pores to give a very smooth surface. The paper thus has a very low porosity and a high degree of resistance to grease and oil.

Velocity gradient

This is an alternative term for the shear rate.

VFA

This is an abbreviation for volatile fatty acid.

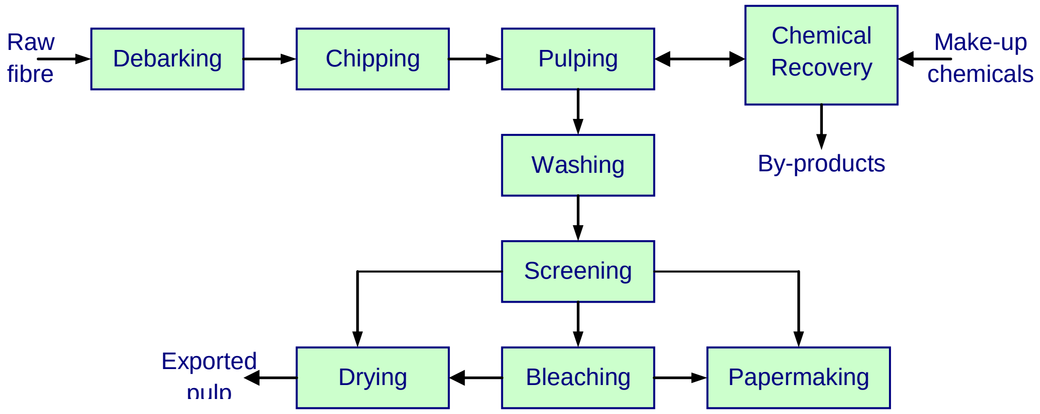
Virgin pulps

This is one of the two broad categories of fibrous papermaking pulps (the largest single type of raw material used in papermaking), the other being recycled pulp. Although the gap is closing, virgin pulp is still the larger of the two pulp categories with a global production of about 190M tonne in 2000.

Virgin pulps can initially be classified in two ways:

- in terms of the source of the raw fibre, the main categories being:
    - wood pulps, which account for over 90% of the pulps used in papermaking and are widely used in all papermaking countries
    - non-wood pulps, which account for nearly all the remainder, but their use is concentrated in certain countries such as China
    - synthetic pulps, very small quantities of which are also used in some speciality grades such as tea-bag paper.
- in terms of the type of pulping process, the two main categories being:
    - mechanical pulps, which account for about 20% of the total
    - chemical pulps, which account for the remainder and are dominated by Kraft grades.

All types of pulping process, although differing greatly in the details of the actual pulping stage, have a similar set of auxiliary processes as shown in the block diagram below. Chipping is not done with groundwood mechanical pulping processes and, of course, chemical recovery is only practised at mills with a chemical process. Some smaller chemical pulps mills (notably based on non-wood fibres) have no chemical recovery.



Both wood and non-wood pulps contain the same four basic substances or groups of substances:

- cellulose, the main component responsible for the inherent strength of fibres
- hemi-celluloses, the second largest component that may also contribute to strength
- lignin, the chemically-complex binding material that is also responsible for the brown coloration
- extractives, the minor fraction that is of no value in papermaking.

When looking at quoted data for pulp characteristics, it should always be born in mind that there are significant differences not only between different species within a broad category (such as within hardwoods and softwoods), but also within a species depending on growing conditions, genetic factors, etc. On different days, this can lead to quite significant differences in the exact characteristics of the raw fibre entering a pulp mill, which may be lessened or magnified by the pulping process depending on the level of process control applied.

Visco-elasticity

This is a rheological term applied to certain non-Newtonian fluids, which have a delayed elastic response to an applied stress, ie they have both viscous and elastic properties. One characteristic of such liquids is that, instead of forming a vortex around an impeller when stirred, they may climb up the impeller. In papermaking, visco-elasticity is present in some coating mixes due to their particular rheological characteristics. Visco-elastic materials are characterised by having a "relaxation" time (the time taken to recover from the deformation) which is measured in seconds or tens of seconds compared to the infinitesimally short time for liquids and the infinitely long time for solids.

Viscosity

This is an important characteristic of liquids in terms of their rheological properties. The viscosity of a liquid is its internal resistance to flow caused by friction from the attractive forces between the liquid molecules. The normal viscosity measurement is the dynamic viscosity measured as the shearing force (Newtons) per unit area required to produce a velocity gradient of 1 second^{-1}. The unit of viscosity is the Poise (P), which has the units of 10^{-1} Newton.second/m^2 (identical to kg/second.m or Pascal.second). It is more common for aqueous liquids to use the centipoise (cP), which has the units of 10^{-3} Newton.second/m^2 or mPa.second. The kinematic viscosity is the dynamic viscosity divided by the density with units of m^2/second. Liquids are described as Newtonian when the viscosity is independent of the shear rate. One example of a non-Newtonian liquid is a thixotropic liquid, where the viscosity decreases with shear time (see rheology for further discussion of this).

The viscosity of water has the value of 1 cP at 20^{o}C, but decreases with temperature spanning the range of 1.8 cP at 0^{o}C to 0.55 cP at 50^{o}C and 0.28 cP at 100^{o}C. It is strongly influenced by the presence of dissolved and particulate materials depending on their interaction with the water molecules. For charged suspensions, there is an electro-viscous effect which increases the viscosity due to the extra energy required to overcome the interactions between charged species in the electrical double layers. For charged polymer solutions, this effect is small, but, as the hydration of the polymer depends on its chain length, viscosity measurements can be used to estimate their molecular mass from the formula:

$$\text{Polymer viscosity} = k\,M^x \text{ where } k \text{ and } x = \text{constants and } M = \text{polymer molecular mass}$$

Viscosity measurements can also be used to estimate the consistency of suspensions as any inter-particle interactions (eg network contacts between pulp fibres) or interactions with water (eg hydrogen bonding) influence the mobility of the liquid. As this effect is very dependent on measurement conditions, it is usually referred to as the "apparent viscosity" (see this example of the effect of liquid viscosity on the extent of fibre flocculation).

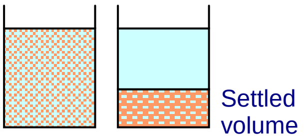
The significance of viscosity in papermaking depends on location:

- ☐ at the wet end in relation to the ease of water removal from the paper web
- ☐ at the size press and coater, in relation to the pick-up and penetration of the applied solution/suspension into the base paper.

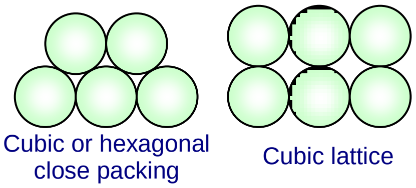
Void volume

This is the proportion of a body that is not occupied by solid matter. It is an important characteristic in the following areas:

- for the forming paper web as this is one of the many factors that influence web permeability and drainage rate
- for some minerals that are used as wet end fillers such as precipitated calcium carbonates and calcined clay, where the particle morphology is such that there are internal voids within the particles and this accounts for some of their light-scattering ability.
- for minerals that are used as coating pigments, where it is usually desirable to use the maximum solids content in the coating that is consistent with the target coating quality, but also to minimise the binder demand and the drying energy. As the pigment accounts for the bulk of the coating by weight, the minimum water content in the coating mixture is determined by a combination of the inherent water content of the other coating additives and the packing ability of the pigment particles. The latter is determined by allowing the pigment to consolidate by settling and the void volume is then the fractional volume occupied by the pigment solids in the settled volume.



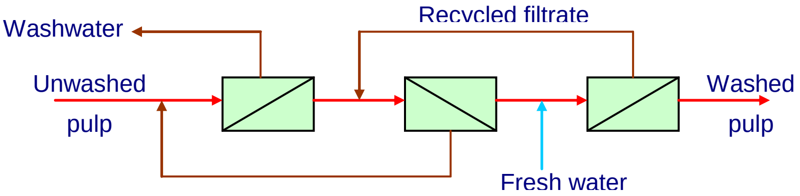
From a theoretical viewpoint, the maximum packing density of solid objects is determined by their particle size distribution and shape. For spheres of the same size (100% monodisperse), the closest packing possible is either cubic or hexagonal packing (see picture at near right), where the spheres occupy 74% of the total volume. Another type of packing for equal-sized spheres is a cubic lattice, but this has a lower packing density where the spheres occupy 52% of the total volume. For some polydisperse solids, the packing density can be greater than these values when there are small particles that can fit into the voids. In practice, for real solids (like all mineral pigments used for coating), the packing density falls short of these maximum levels and ranges from about 43% for fine kaolins (due to their anisometric character), 50% for coarse kaolins, PCCs and titanium dioxide and up to nearly 70% for natural calcium carbonates.

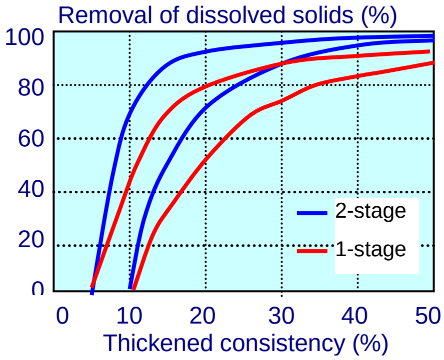


Washing

This term is applied to processes in pulping, bleaching and deinking that remove dissolved substances from the pulp. When it is applied towards the end of these processes, it is very important in terms of paper chemistry as it removes substances from the pulp that may cause problems on the paper machine. It is usually accomplished simply by thickening the pulp to increase its consistency. The term thickening is often used interchangeably with washing, but the emphasis in pure thickening is on removing water for economic reasons (eg to lower the water load on final dryers or on a high temperature treatment stage such as disperging within a deinking process) rather than on removing the dissolved substances. Washing efficiency may be augmented by the addition of chemicals, but this is not common.

Washing is essential within pulping, bleaching and deinking processes in order to separate water circuits, particularly where different chemistries are used, eg between the alternating acid and alkaline stages in the bleaching of chemical pulps and, in deinking, between the normally alkaline flotation stage and the more neutral or slightly acidic washing stages. Potentially, washing is a very water-intensive process so it is normal practice to re-use water in a counter-current fashion, where the filtrate from one stage is used to dilute the pulp in the previous stage (see diagram below for a 3-stage process). Where the chemistries of adjacent stages are very different (eg acid and alkaline), the counter-current movement of water can omit one stage (so-called jump-stage water recycling).





The removal of dissolved solids may be easily modelled in terms of the initial and final consistencies and the number of washing stages. In the example shown at left, it is assumed that there is no fibre loss in the filtrates and that fresh water is used as the dilution water in the single stage and at the second stage of the 2-stage process. Filtrate from the second washing stage is recycled to the first stage as indicated in the process diagram above (although this is somewhat less effective than a fully-open water system). It is evident that a 2-stage process is more effective than a single stage - for example, dewatering a pulp at 10% initial solids content to 50% in a single stage removes about 90% of the dissolved solids, whereas a similar removal is achieved by dewatering the pulp to 25-30% in 2 stages.

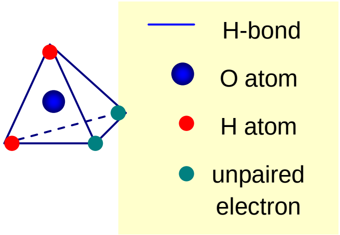
Actual washing practices do vary between different types of pulp:

- ❑ mechanical pulps are usually washed but in many cases not that thoroughly, although this is improving, particularly after the pulps are bleached (see this example)
- ❑ chemical pulps are usually washed quite thoroughly, again particularly after each bleaching stage, but washing of some unbleached pulps can be difficult
- ❑ deinked pulps are also usually washed quite thoroughly, sometimes with added surfactants
- ❑ broke is rarely washed before the repulped stock is returned to the machine system, unless it has been treated chemically in some way, eg decolorised.

Washing efficiencies tend to be highest on machines producing market pulp for transport to another site as the pulp then has to be thickened to the maximum extent in order to minimise final drying costs. In the absence of this pressure, final pulp washing at integrated mills tended to be neglected, but this attitude has changed with the realisation of the adverse effects of dissolved solids carry-over. However, one of the issues in improving pulp washing efficiency is what to do with the increased quantity of dissolved solids that have been removed in this way. This is discussed further under biological treatment.

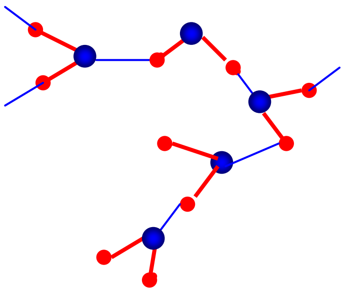
Water

Water (H_2O) is an essential ingredient in papermaking, but it tends to get taken for granted due to its low cost and ready availability at most locations. Superficially, water is used in papermaking for transportation, cleaning, chemical preparation, etc, but its presence during stock preparation and sheet forming has a profound effect on the properties of the final sheet of paper. The water medium allows the fibres to swell and become flexible, thus allowing close conformation once the water begins to be removed. The water used on the paper machine is a mixture of fresh water and water recycled after some previous use.



At first glance, water is a very simple molecule, but in actuality it is very complex and its precise size and detailed structure depend critically on its form as a solid (ice), liquid or gas. The oxygen in liquid water is normally considered to be sp^3 hybridised such that the water molecule should have a tetrahedral structure with the divalent oxygen at the centre and the two hydrogens and two electron pairs at each of the four corners (see picture at right). Although this structure is helpful to visualise the bonding arrangements, this is not thought to be absolutely correct although there is some hybridisation within the molecule. The O-H bond length varies with form, but is about 0.1nm in water and the overall molecule, although not a perfect sphere, is about 0.3nm across.

Despite this uncertainty, the key to the structure and properties of water is the extensive hydrogen bonding between molecules, which is greatest in the various forms of ice, but still present in the liquid. Water is thus not an assembly of separate H_2O molecules, but several H_2O molecules are associated with one another to give an extensively-linked structure, where the forces extend over quite a distance, ie are not just between adjacent molecules. The strength of the hydrogen bond in water is about 23 kJ/mole compared to about 500 kJ/mole for the covalent O-H bond and about 1 kJ/mole for the van der Waals O-H attraction. The diagram at left shows just one hydrogen bond per oxygen atom, but there can be two depending on temperature. The hydrogen bonds in water are reckoned to be about 90% ionic and only 10% covalent. Hydrogen bonds are still present even in water vapour.



Many of water's properties originate from its hydrogen-bonded structure, the more important ones in relation to paper chemistry being:

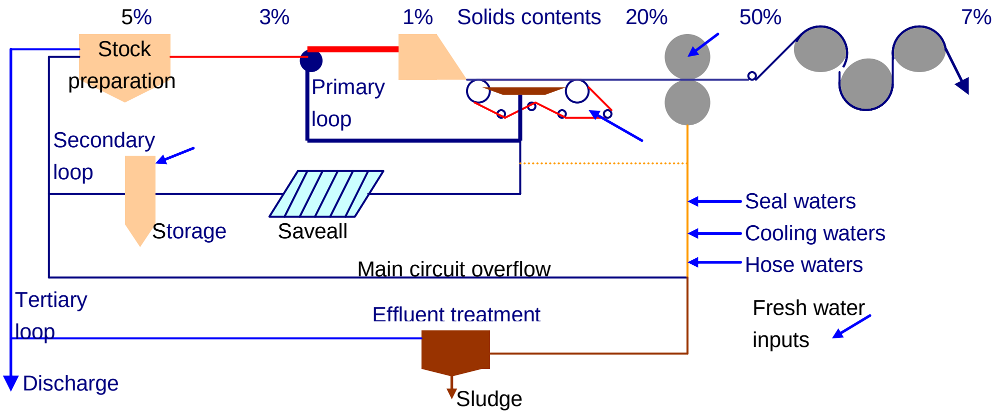
- its solvent abilities, which are due to its small size and high dielectric constant (about 80). This makes water an excellent solvent, particularly for other polar molecules such as electrolytes, as it reduces the electrostatic attractive forces holding the ions together in the solid state.

- its surface tension (73 mJ/m$^{2)}$ at 20°C), which is relatively high due to the strong inter-molecular attractive forces from hydrogen bonding. This property is important in relation to surface wetting phenomena and related topics such as adhesion and sizing.
- its viscosity, which is again due to the strong inter-molecular attractive forces from hydrogen bonding. The viscosity of water is 1 cP at 20°C, but decreases with increased temperature (to 0.47 cP at 60 °C) due to the weakened hydrogen bonding.
- its specific heat (4.2 J/g.°C), which is again high due to the energy required to overcome the hydrogen bonding as the temperature rises.
- its dipole moment (6 x 10^{-30} C.m or about 3 Debye units in the liquid state), which arises from its non-linear structure and polar character. Water's dipole moment is the reason why it absorbs microwave energy so effectively, but it is quite small as the extensive hydrogen-bonding lowers the charge difference between the hydrogen and oxygen atoms.

The characteristics of pure water are, of course, modified considerably by the presence of dissolved substances in fresh water and from dissolution within the papermaking system.

Water closure

This term is used to denote the use of less fresh water at the wet end of the paper machine, which then results in a smaller flow of wastewater for external discharge. Water use at the dry end of the paper machine is much smaller and limited to the water used for preparation of the solutions and suspensions for any surface application equipment present. Whereas only a relatively small fraction of the water at the wet end is evaporated during drying, all of the water applied to the paper surface is removed by evaporation. A typical, but very simplified, water system at a paper mill is illustrated below.



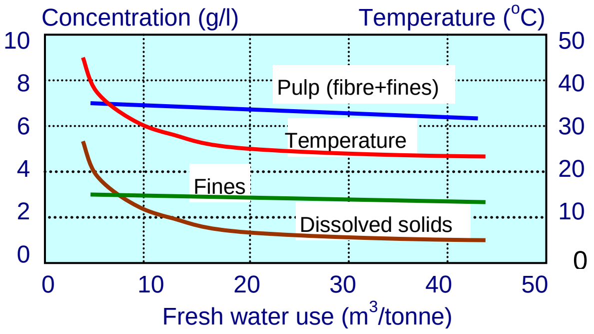
Ultimately, closing up at the wet end would result in a situation of zero effluent discharge outside the mill, although small quantities of water would still be discharged with other solid waste streams leaving the site (eg rejects and sludges). There are a number of mills throughout the world that have achieved this situation, mainly in the sector making recycled packaging papers. The driving force for closing up is usually environmental, but it is the resultant changes within the process that dictate just how far this can be taken. For most mills, the optimum degree of water closure is well short of zero discharge, but this is ultimately an economic decision as technologies are available to render all used machine waters suitable for re-use.

There are many different ways that a paper machine's water system could be closed up, detailed discussion of which is outside the scope of this document. For the purposes of the discussion here in relation to the impact of wet end water closure on papermaking chemistry, there are essentially two different approaches to closing up:

- closing up within the paper machine circuits (the primary and secondary loops shown above) so that the total wastewater flow is reduced in line with the reduction in fresh water intake. This is sometimes referred to as internal closure. Normally, most mills would have some form of wastewater treatment plant to which this reduced flow of wastewater would be directed. The great advantage of this approach is the potential improvement in the total retention of raw materials applied at the wet end (see here for an illustration of this).
- closing up by the recycling of treated wastewater (the tertiary loop shown above), in which case the flow to the wastewater treatment plant could remain constant or could even increase. This is sometimes referred to as external closure. This approach would not have the benefit of increased total retention (as some of these substances are removed during wastewater treatment before the water is returned), but it would have the benefit of not increasing the circuit concentrations as much as by internal closure.

Within both these approaches, there are many variations possible, but the important impact within wet end chemistry is the effect of water closure on the circuit concentrations and temperature. As discussed under modelling, the two most important factors determining the material concentration for any fixed input of material into the papermaking system is the degree of water closure and the material's single pass retention. The example illustrated below is based on the same input data as shown here for total retention, but expressed below as circuit concentrations.

Closing up over the range shown here has a negligible effect on the build-up of pulp fibre (SPR = 95%) and a modest effect on fines (SPR = 50%), which together increase total pulp consistency by only about 5%. (This calculation assumes a pulp fines content of 30%.) However, the proportional change in concentration of dissolved solids on closure is more than an order of magnitude greater than for the particulate solids (in the case illustrated, from about 1 to 5 g/l).



This calculation assumes a constant input of dissolved solids (from all sources other than the fresh water itself) of 2% (20 kg/tonne) of the pulp input. In practice however, the degree of closure itself is very likely to change the input of dissolved solids load in some way, for example:

- for the solids originating from dissolution of substances entering the system with pulps/broke.

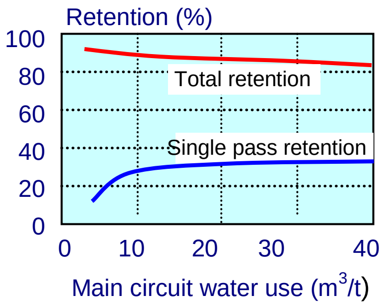
  The increased temperature on closing up could increase the dissolution of both organics and salts, but an increased electrolyte concentration may then have a negative feedback effect on the dissolution of organics (see this example for the effect of conductivity on carbohydrate dissolution from bleached Kraft pulps, this example for the effect of temperature on dissolution from CTM pulps and this example for the effect of contact time on dissolution from recovered papers).

- ❑ for the solids originating from non-adsorption of wet end additives.

  The process of adsorption depends on several aspects related to the chemistry of the dissolved solids, such as the level of electrolytes which generally reduces adsorption (see this example for polyacrylamide). Temperature may also influence adsorption if it affects the solubility of the adsorbate and/or its conformation (see this example for cationic starch).

It is important to note that the degree of water closure does not change the contribution of dissolved solids from the fresh water itself to the concentration of wet end dissolved solids, ie the baseline chemistry remains constant as fresh water use is reduced. In the above example, the baseline levels in the fresh water have been taken as zero except for temperature, for which a value of 15°C has been used.

It is certainly normal to observe an increase in the concentration of dissolved solids on closing up, but, in view of the complexity of the possible interactions, this may be more or less than that predicted in the constant load model above. The increase in temperature seen in the above figure is parallel to the increase in dissolved solids concentration as the thermal energy is assumed to follow only the liquid phase. There is no uncertainty about this build-up curve provided that the energy dissipated at the wet end remains constant. The degree of water closure is also relevant to the equilibration time of the system as the average retention time of any substance with low single pass retention (eg the dissolved solids) rises with increased closure. In combination with the increased temperature on closing up, this also means that the likelihood of the dissolved materials being changed by chemical or microbiological action is much greater on a machine with a more closed water system.



Returning to the subject of water-soluble wet end additives, it is possible to model the impact of water closure on their retentions, but this is more complex than for a material that is associated 100% with either the particulate or liquid phase. In the example shown here, it is assumed that 90% of the additive is adsorbed on the pulp fines, which itself has a single pass retention of 60% (see this example for the effect of adsorption at a constant degree of water closure). The total additive retention increases on closing up in line with the expectations from the general trend shown here, but its single pass retention gets progressively worse. The reason for this is that the dissolved fraction of the additive builds up to a greater extent on closing up than does the adsorbed fraction. This means that the SPR of the total additive thus trends towards the SPR of the liquid phase, which is very low. This model should hold true for wet end additives that are stable, but it is probably too optimistic for other additives such as those that are biodegradable like starch. Closing up increases the potential for microbial activity, one effect of which could be the breakdown of adsorbed starches, which would lower both single pass and total starch retentions.

From the foregoing discussion, it is evident that the degree of water closure has a very significant impact on the chemical status of the wet end. The principle primary changes (increased temperature and concentrations of dissolved solids and fines) bring about secondary effects such as decreased water viscosity, higher solubility of most electrolytes, reduced solubility of gases, etc. The final impact on process chemistry depends on the net outcome of these changes, some of which reinforce one another (eg higher temperatures lead to lower levels of dissolved oxygen and greater starch dissolution from broke, both of which will expedite the potential for undesirable anaerobic conditions to develop), whilst others negate one another to some degree (eg better drainage from decreased water viscosity, but impaired drainage from higher retained fines). These interactions are quite complex and are summarised in the table below.

Overall, it is evident that internal water closure has the potential to deliver significant environmental and cost benefits (better use of raw materials, less reliance on wastewater treatment and reduced sludge arisings), but the implications for process chemistry are challenging in terms of maintaining acceptable runnability and product quality.

SUMMARY OF CHEMISTRY ISSUES ON INCREASED WATER CLOSURE

Primary effect	Final benefit	Final problem
Increased temperature	Less severe microbiological problems? Easier water removal	More severe microbiological problems? Higher concentrations of problematic substances Tackier deposits Increased hydrolysis of sizes Increased scaling ($CaCO_3$) Lower DO levels and more anaerobic activity
Increased dissolved solids concentrations	Higher total retention of dissolved solids	Adverse effect on retention aids Increased corrosion/scaling Increased microbiological activity Increased foaming Odour problems
Increased fines concentrations	Higher total retention of fines Improved ply bonding	Impaired drainage Impaired product quality?

Water disinfection

Disinfection of the process water is an important component in minimising microbiological problems caused by proliferation of bacteria and/or fungi within the machine circuit. The most common disinfection processes are still based on either chlorine gas or sodium hypochlorite, but the use of chlorine dioxide, sodium bromide/hypochlorite, chlorine/bromine release compounds and ozone is increasing. The reasons for this shift depend on local factors, such as water pH and organic content plus environmental concerns about generating chlorinated organics and safety in storage and handling of chlorine gas. The disinfecting power of hypochlorous acid is much greater than that of the hypochlorite ion, so chlorination is most effective at pH values below the pK value (about 7.5) and preferably below pH 7. One of the advantages of bromination over chlorination is that hypobromous acid is the weaker acid and thus maintains a higher proportion of unionised halogen at lower pH values, ie is more effective at typical water pHs than chlorination (see this figure)

Chlorine has a strong tendency to react with chemicals present in the water, particularly organics and ammonia. It is necessary to satisfy the chemical demand before a reliable chlorine residual can be maintained for protection against bacterial re-growth downstream. The presence of organics can lead to the generation of chlorinated organics (AOX), but usually at very low levels. Chlorine reacts with ammonia to form a series of chloramines, which are much weaker disinfecting agents than chlorine, but are longer-acting. "Breakpoint" chlorination is the addition of adequate chlorine to oxidise ammonia fully to nitrogen.

The use of oxidising disinfectants can have other benefits such as reducing the concentration of dissolved iron or manganese ions, a particular problem in rivers receiving discharges from working or abandoned mines. Non-chemical disinfection is possible by the use of, for example, ultra-violet irradiation and this technique is used by one or two mills for special applications. The need for effective disinfection is greatest at mills with neutral on-machine pH. On such machines, the natural river flora would be able to grow relatively rapidly, whereas acid conditions would exercise some control as a low pH is inimical to growth of most (but not all) river micro-organisms.

Water removal

This term is used to describe the various processes that remove water from the papermaking stock after the paper web is formed and then consolidated. It is broken down into three stages:

- ❑ drainage initially by gravity and then by vacuum assistance on the formation wire
- ❑ pressing against absorptive fabrics ("felts") in the nip between two large press rolls.
- ❑ final drying against steam-heated drying cylinders.

The term "dewatering" is also sometimes used to cover both the drainage and pressing phases.

The ease of water removal is influenced by many attributes of the papermaking stock and the design/operation of the paper machine from the flowbox slice onwards. The pulp component of the papermaking stock is unique in its ability to hold onto water through hydrogen bonding. Therefore, in order better to understand the processes of water removal in papermaking, it has proved useful to sub-divide the stock's total content water into several categories depending on their ease of removal from the pulp and on their freezing characteristics:

- ❑ unbound water, which is further sub-divided into:
    - water outside the fibre wall, which is the bulk water in the suspension.
    - water held within macropores of the fibre wall, which freezes at the same temperature as the bulk water outside the cell wall.
- ❑ bound water, which is further sub-divided into:
    - water within micropores of the fibre wall, which freezes at a lower temperature than the bulk water.
    - water which does not freeze at all and is considered to be hydrogen-bonded to the hemi-celluloses and cellulose. It can be calculated that cellulose itself has a solids content of about 75% when each of its hydroxyl groups is associated with one water molecule (see this table which gives very similar levels to this for an unbleached Kraft pulp), but most of the cellulose hydroxyls are already hydrogen-bonded either intra- or inter-molecularly.

The external unbound water is largely removed during the initial drainage stage and the drainage rate is mainly influenced by the ease of passage through the particulate matrix, ie by its external pore structure which is determined by the particle size distribution and fines content. Pressing involves the removal of residual unbound water, but this is still strongly influenced by the structure of the particulate matrix. High-temperature drying is necessary to remove most of the bound water and this is more influenced by the detailed chemistry of the paper web, but a more open structure should still allow easier passage of water vapour. The relationship between these different forms of moisture is shown for an unbleached Kraft pulp under drying.

Water retention

This term is used in two different areas of papermaking:

- in aqueous paper coating in relation to the ease of water penetration from the added coating into the base paper - this is controlled by the use of water retention agents in the coating formulation
- in papermaking in relation to the swelling characteristics of fibres - the pulp's water retention value is one method of quantifying this property.

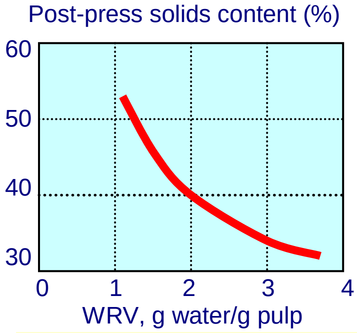
Water retention agent

This type of chemical is used in aqueous pigment coating to control the penetration or migration of water from the coating mix into the base paper. It is particularly important in coatings with a high proportion of latex binder due to the latter's low viscosity and in coating's with a high proportion of calcium carbonate pigment, which holds on to water less than do clays. If migration of water is too rapid, it causes fast immobilisation of the coating solids leading to possible poor coating uniformity and streaking. It can be controlled by the addition of chemicals such as starches, CMC, alginates and acrylates and, by the nature of these chemicals, they will also influence the overall rheology of the coating mix.

Water retention value (WRV)

This is one of two techniques (the other being solute exclusion to give the fibre saturation point) that is used to measure the swelling ability of fibres. The technique is simply to centrifuge the pulp sample (at 3000g) for 15 minutes and determine the water content of the resultant pulp plug. This is the pulp's WRV in units of g water/g fibre. The values vary from about 1 g/g for mechanical pulps to over 2 g/g for chemical pulps, ie the centrifuged pulps have solids contents of about 30% to 50%. The WRV is usually greater than the FSP value as shown in this table.

It might be expected that the WRV should also be relevant to the processes of water removal, particularly during pressing. This has been confirmed in a study spanning 60 furnishes of widely differing pulp types and levels of refining (see figure at right). The practical importance of this study is that pulps with a high WRV also have a high swelling ability, which is a positive attribute for paper strength, but, as shown here, less desirable from the viewpoint of machine productivity. It is thus important not to develop strength in pulps that is not needed in the product (eg by over-refining) as this will adversely affect productivity.



Source: Springer, A in Tappi J., 1991, 74, 4, 221-228.

In the same study, the WRV was used as an indicator of the pressability of a bleached softwood Kraft pulp in relation to the effects of added chemicals. The effects of a range of retention/drainage aid polymers was small in most cases, but two polymers of relatively high cationicity did lower the WRV by about 10%, ie from a post-press solids content of 45 to 50%. This seemingly-small increase would be very significant in terms of reduced final drying costs.

Waxes

This is a generic term for the esters formed between higher alcohols and higher fatty acids, which take the general form $R_1CO_2R_2$. Examples are animal waxes such as beeswax (myricyl palmitate) where $R_1 = C_{15}H_{31}$ and $R_2 = C_{30}H_{61}$ and vegetable waxes such as carnauba wax (myricyl cerotate) where $R_1 = C_{25}H_{51}$ and $R_2 = C_{30}H_{61}$. The term wax is also applied to non-vegetable waxes derived from petroleum (eg paraffin wax), which are pure hydrocarbons. Waxes are used in an emulsion form as lubricants in coating formulations and to provide barrier properties in certain paper grades.

Wet end additives

Most raw materials in papermaking are added at the wet end of the paper machine, but this does vary quite considerably with the grade of paper being made. The proportion of wet end added materials varies from about 70% for light-weight coated papers to 100% for grades such as newsprint and tissue/towel. On all paper machines, fibrous materials from pulps are the dominant material added to the wet end and, on some paper machines, pulp is the only material in the product, eg newsprint.

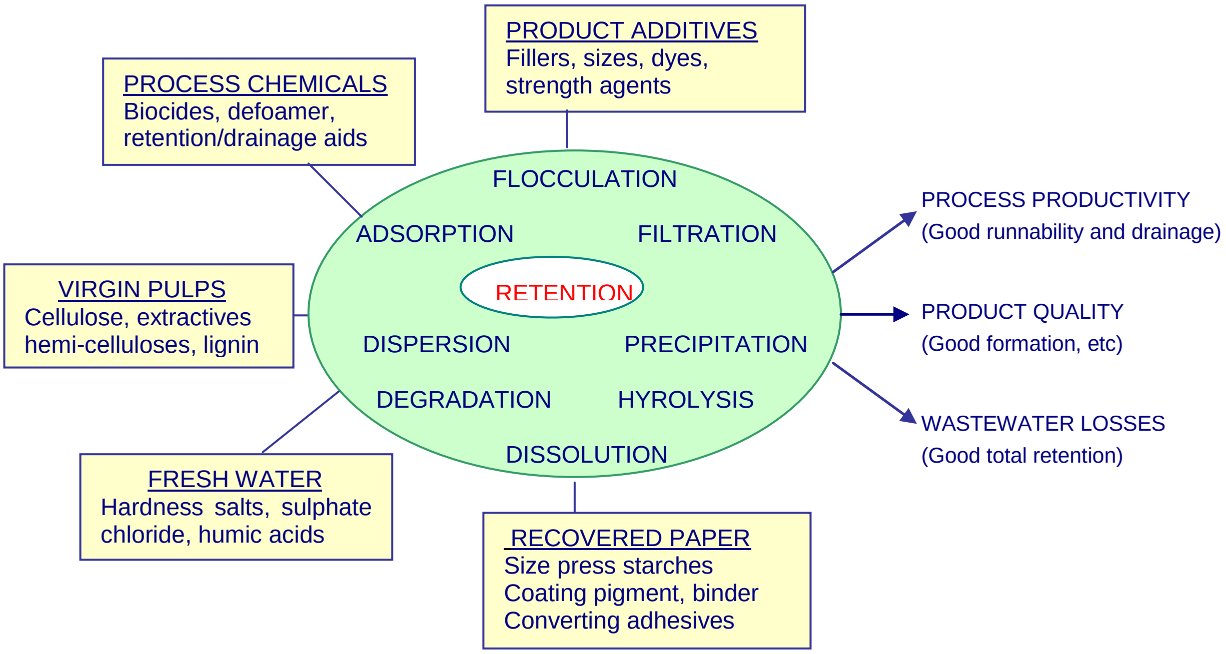
Non-fibrous raw materials account for the remainder of materials added at the wet end and for 100% of surface-applied materials. Fillers account for the bulk of non-fibrous wet end additives, but are only used in grades where the paper surface is used to convey information in printed or written form. Excluding fillers, other non-fibrous wet end additives account for a small proportion of the product in most cases (below about 2%), the highest levels being where wet end starch is being used (often to replace size press addition, such as on recycled fluting grades) or, in some rather special cases, where high dye additions are needed to make very deep-coloured papers.

The most important distinction between different wet end additives is their form, notably whether they are present as insoluble particulates (eg pulp, filler) or in the dissolved state through being water-soluble (eg starches, wet strength agents, dyes, etc). This distinction is important because of the different retention mechanisms for particulate and dissolved solids. Particulate materials are retained by a combination of aggregation of fines followed by filtration/sieving on the formation wire, whereas dissolved solids are retained either through being adsorbed by the particulate matrix or by simply being carried into the drying section in the water remaining in the paper web. Of these two mechanisms, adsorption is the most effective by far as the adsorbed solids then have the same single pass retention as the particulates on which they are adsorbed, whereas the single pass retention of non-adsorbed dissolved solids is always very lower (about 1% depending on the water balance at the wet end).

Wet end chemistry

The chemistry of the papermaking process can be divided into that taking place at the dry end of the paper machine (dry end chemistry) and that taking place at the wet end, the dividing line between them being somewhat arbitrary. Wet end chemistry is defined in this document as the chemical interactions that take place between all components of the papermaking furnish from the pulper through to the end of the press section, including any changes occurring during water recycling. The key objective within wet end chemistry is:

> "to optimise the state of association of the whole papermaking furnish in order to maximise its retention characteristics concurrent with achieving an optimum sheet structure (formation, even-sidedness, etc) and acceptable machine productivity (drainage, runnability, etc)."



The term ”association” embraces two critical types of interaction – the aggregation of particulate solids and the adsorption of dissolved materials. This optimum retention can be defined as the maximum, stable retention value achievable by balancing primary (single pass) retention on the formation wire plus secondary recovery in savealls and by water recycling against the major product constraint of acceptable sheet formation/uniformity. Wet end chemistry is thus intimately tied up with water management on the machine.

Optimising wet end chemistry is about maximising the desirable processes in the summary figure below (adsorption, flocculation and filtration), whilst minimising the undesirable ones (dispersion, precipitation, degradation, dissolution and hydrolysis). Wet end chemistry can be broken down into three sorts of chemistry:

- reaction chemistry
  This is where chemical reactions lead to new chemicals, but this is very limited in papermaking as most chemicals are purchased in a fully-functional state. There are exceptions, but these take place during dry end chemistry. The only chemical reactions taking place at the wet end are undesirable ones related to various problematic substances and the hydrolysis of additives such as AKD and ASA sizes.

- microbiological chemistry
  This is similar to reaction chemistry in that it leads to new chemicals, but only through the agency of micro-organisms. Biodegradable organic (eg starches) and inorganic (eg sulphate) substances are transformed to other substances and energy made available for microbial growth. This occurs to some degree on all paper machines and is probably more prevalent than reaction chemistry.

- colloid chemistry
  This is the chemistry of small particles and large macro-molecules and is the most important aspect of wet end chemistry.

Wet end interactions

There are many different interactions possible at the wet end, which can be classified in relation to the types of materials involved:

- ❑ particle-particle interactions, particularly those involving the fines fraction where we are mainly interested in achieving an optimum degree of aggregation in relation to retention, drainage and paper formation
- ❑ particle-solute interactions, the most important of which is the managed adsorption of additives onto the particle surface, but the reverse processes of desorption and dissolution are also important, usually from the viewpoint of minimising their occurrence
- ❑ solute-solute interactions such as precipitation reactions between inorganic ions or between oppositely-charged polymers, eg cationic polymers with anionic trash.

Many of these interactions are charge-mediated, but some may involve hydrogen bonds or purely mechanical forces.

Wetness

This term is applied to the drainage of water from pulps and is the opposite of freeness.

Wet strength

Wet strength is the ability of the paper to resist disintegration when saturated with water. In the absence of specific chemical treatment to enhance wet strength, paper retains less than around 10% of its dry strength when wetted. Wet strength should not be confused with sizing, which only slows down the absorption of water and has no substantive effect on wet strength. The poor wet strength of normal (ie non-wet strengthened) paper products affirms the fact that much of their dry strength is attributable to hydrogen bonding between the cellulose units and is thus easily disrupted by water molecules. The strength of the paper web during the processes of water removal is important in terms of process runnability - this is the wet web strength, which is not the same as the wet strength of the final product.

The main types of paper requiring some wet strength are towelling products, facial tissue, label paper, filter paper, photographic paper, tea-bag paper, wall paper, banknote paper and some packaging papers/boards used for packaging wet (damp) products or for resisting moisture in use (eg sack papers). The mechanism for giving paper the property of wet strength is to protect the inter-fibre bonds from disruption by water through the incorporation of wet strengthening agents. As most wet strength agents do not cure fully on the paper machine, it is customary to check the resin's efficacy by carrying out an accelerated curing test on the paper at 105^{o}C for 5 minutes or at 80^{o}C for 30 minutes.

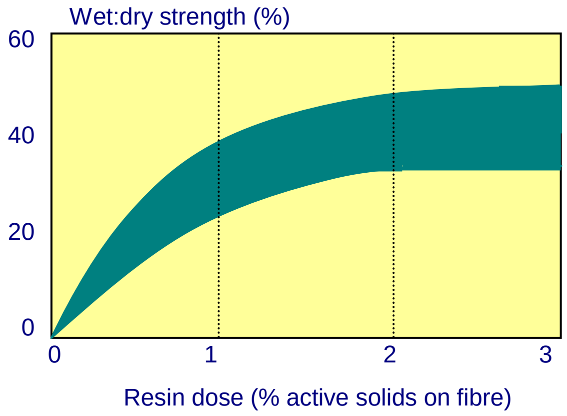
Wet strength agents

The main type of wet strength paper used to be vegetable parchment, which is made by post-treating the paper with sulphuric acid. This changed with the development and application to paper of thermosetting resins, initially those based on formaldehyde condensation products with either urea (UF resins) or melamine (MF resins). In the 1950s, the polyamidoamine-epichlorhydrin (PAE) resins were developed and these had the advantage of curing under neutral pH conditions in contrast to the acid conditions needed for the UF/MF resins. For similar reasons driving the move to neutral sizing, there has since been a gradual shift to using the PAE resins with the additional motivation of there being no handling constraints related to the presence of formaldehyde. Wet strength can also be introduced by the addition of polyethyleneimine and some latices at the wet end or by surface treatment of the paper with a cross-linking chemical such as formaldehyde. One of the latest type of wet strength chemicals is based on polyisocyanates.

These reactions to confer wet strength take place only at the elevated temperatures in the drying section of the paper machine and are thought mainly to be due to homo-reactions between the resin components to surround the paper components with an impenetrable, 3-dimensional matrix rather than to hetero-reactions of the resin with the fibre. The principle wet strength resins (the UF and PAE resins) are both aqueous solutions as applied to the paper machine, so their most critical characteristic for good single pass and total retention is the ability to adsorb on the particulate matrix. This is normally achieved by charge attraction, so the dominant form of all wet strength resins is a solution of cationic polymer.

The UF/MF and PAE resins are the principle wet strengthening agents used today for conferring permanent wet strength on the paper. However, it can be useful in certain applications for the wet strength to be lost after a certain contact time with water, eg tissue/towel papers so that they can be flushed away afterwards. The main chemicals used to give this temporary wet strength are the glyoxalated-polyacrylamide derivatives and certain starches such as dialdehyde starches and blocked reactive group starches.

A guide to the overall performance of wet strength agents under conditions of good cure is shown in the figure at right. It is not possible to retain more than 50% of the dry strength when wet and 20-40% is more normal. It should be noted that some resins improve the dry, as well as the wet, strength of the paper, but this may be due to changes in fines retention and formation as well as direct effects of the resin on inter-fibre bonding. The characteristics of the four main types of wet strength agent are indicated in the table below.



Property	UF resins	MF resins	PAE resins	GPAM resins
Type of wet strength	Permanent	Permanent	Permanent	Temporary
Effective pH	3.5-5	4-5.5	5-9	4-7
Cure at reel (%)	20-30	60-70	30-50	70-90
Full curing time (days)	< 30	< 20	< 15	< 2
Broke handling	pH 3-4, high temp	pH 3-4, high temp	Hypochlorite, high temp	Alkaline, ambient
Specific problems	Formaldehyde	Formaldehyde	Hypochlorite at wet end, chlorinated organics	Sulphite, bicarbonate at wet end

Wetting

A surface is considered to be fully wetted when the contact angle is zero, but only partially wetted when the angle is greater than zero. In practice, most surfaces have a positive contact angle and are partially wetted by most liquids. This concept is related to the topics of interfacial energy or tension, liquid spreading and adhesion.

Wet web strength

This is the tensile strength of the paper web during the processes of water removal and is very important to the runnability of the paper machine. The wet web strength increases progressively as the web solids content increases during water removal, but tends to be most critical in the area of the press section as this is the location where the paper web may first be unsupported by a carrying fabric (the term "open-draw" is used for when this occurs between pressing stages). Good drainage on the formation wire is thus desirable not only because this is the most economical way to remove water, but also because the paper web is then stronger during pressing, eg a 1% decrease in sheet moisture corresponds approximately to a 10% increase in web strength. Wet web strength is particularly important on paper machines making wood-containing grades due to the relatively low strength of mechanical pulps (see groundwood pulps).

Wheat starches

These are a common type of starch used in papermaking. They have a lower amylopectin content than potato starches and contain some fatty material (see this table for comparison with other starch types). The fatty content contains very little free fatty acids (compared to maize starch), so cannot react with cations such as calcium, but still causes some solution turbidity and increases the gel temperature. Wheat starches do contain about the same level of phosphorous as potato starches, but it is all associated as phospholipids with the fatty material. Wheat starches have the smallest sized granules with a mass average of about 8 µm and a flat, round or elliptical shape.

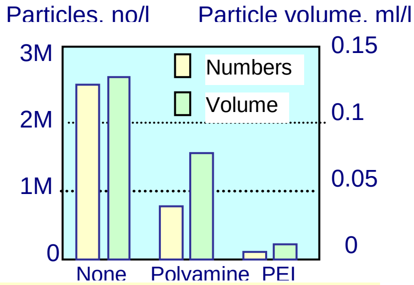
Whiteness

This is an important optical property of some paper products, which is similar to, but not the same as, brightness. There are two whiteness measurements - for outdoor whiteness using the CIE standard D65 illuminant and for indoor whiteness using the CIE standard C illuminant. The main difference between the two procedures is the lower ultra-violet light content in illuminant C compared to D65. Whiteness should ideally be assessed over the whole of the visible spectrum, but, in practice, this is done at just three wavelengths.

White pitch

This is a type of pitch deposit, which occurs on paper machines using coated broke or recovered paper that contains some coated grades. The deposit is usually a mixture of coating latices such as styrene butadiene and polyvinyl acetate. Many coating pigments contain dispersants (typically polyacrylates), which, whilst they cause wet end problems due to their high cationic demand, should help dispersion of the latices during broke repulping. If these are not present, broke pulpability can be augmented by the addition of wetting agents to the broke pulper followed by the addition of an effective retention aid system to the mixed thick stock.

Due to the hydrophobic nature of the latices, it is important to use retention polymers with a certain hydrophobic character (low HLB number) than normal, such as modified polyethyleneimine. An example of this is illustrated at right, which compares a modified polyethyleneimine with a polyamine on a synthetic latex in the presence of TMP. The latex particles were separated using a DDJ and counted by a dye-labelling technique. In addition to the superior performance of the PEI, the comparable decrease in both particle number and particle volume indicates that the retained latex particles were deposited on the pulp without aggregation, which is the desired outcome.



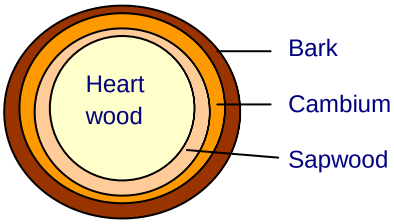
Source: Belouadi in Pulp Paper Canada, 2000, 101, 9, 58-61.

Wood

This is the dominant source of papermaking pulp, accounting for about 92% of total pulp use on a global basis, the remaining 8% being non-wood fibres. Botanically, trees are classified as seed plants (spermatophytes), which are sub-divided into two groups:

- the gymnosperms which have naked seeds and include all softwoods (evergreen or coniferous trees)
- the angiosperms which have encased seeds and include all hardwoods (deciduous or broad-leaved trees).

The cross-section of a tree is divided into various concentric layers, as indicated in the illustration below:



- the outer-most ring of bark is made up of two layers
  - an outer layer of dead corky material, composed of epidermal cells that protect the stem from damage and from drying out
  - an inner layer of live bark, the phloem, which is formed of tall thin tubes, like capillaries, which transport the sugars and other materials made in the leaves to all the other living cells in the tree.
- the thin cambium layer is made of growing cells, which produce fresh phloem (bark) and fresh xylem (wood). The cambium layer slowly moves outwards as the tree increases in girth and the outer bark periodically splits or is shed and is replaced by a new outer layer.
- the innermost, and by far the thickest, layer is the xylem, which is divided into two parts:
  - living xylem cells form the sapwood, which carry water and minerals from the roots to the leaves. As new sapwood is formed the inner-most sapwood cells die and become heartwood.
  - dead xylem cells are the heartwood, which consists of dead material that helps support the tree but has no role in its growth. These cells slowly fill with tannins, resins and other substances, making the wood darker in colour and more resistant to decay and insect attack.

Tree rings within the xylem are found on all trees with an annual growth pattern alternating between a period of slow growth (during the winter) and periods of more rapid growth (during the summer). The cells in the early part of the growing season (Springwood) are large and thin-walled with a rather pale colour compared to the smaller and thick-walled cells with a darker colour in the later part of the growing season (Summerwood). These two rings of light and dark wood represent one year's growth.

In trees, the papermaking fibres are obtained from the vascular (conducting) system which forms the xylem. There are various types of cell within the xylem layer:

- tracheids

  These are long (up to 4mm) tapering cells that run longitudinally along the trunk and are more commonly referred to as fibres. The surface of tracheids usually contains pits, which permit water transport. Tracheids are the dominant cell type in softwoods (90-95% of weight), but are absent from hardwoods. An illustration of a typical tracheid structure is shown below.
- fibres

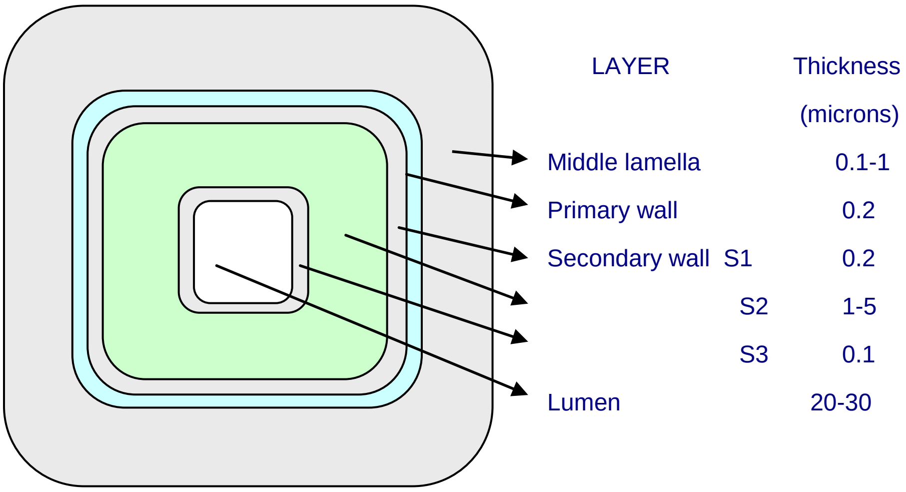
  These are similar to conifer tracheids, but are shorter in length (about 1 mm long) and usually thicker-walled. Like tracheids in softwoods, they run longitudinally along the trunk, but only provide support and have no conducting function. The surface of fibres is usually pitted, but less so than with softwood tracheids. Fibres make up the bulk of the wood in most hardwoods.
- vessels

  These cells form the conducting system in hardwoods and have the shape of broad tubes. They account for usually no more than 10% of the hardwood, but are not present at all in softwoods. The run longitudinally and can extend for several 100 mm.
- parenchyma ray cells

  These are simple cells that store food materials. Unlike tracheids or fibres, they are arranged horizontally, extending radially outwards towards the bark. These are more abundant in hardwoods than softwoods.

Papermaking fibres (or tracheids) are essentially long, slender tubes with a hollow centre (the lumen), the structure and approximate size of a typical wood fibre being as shown in the drawing below. Within the fibre, there is a further sub-classification between variously-sized fibrils. It should be noted that the actual fibre dimensions vary not only between tree species, but also within species dependent on growing conditions, eg between Springwood and Summerwood and between sapwood and heartwood. An important bulk property of woods is their density as this determines the yield of papermaking pulp per unit volume of timber. Hardwoods are usually denser than softwoods with an overall range of 300-600 kg/m^3. The influence of fibre dimensions on the papermaking quality of virgin pulps is discussed under fibre.

Cross-section of softwood tracheid (not to scale)



On a chemical basis, wood is usually broken down into the following four sets of substances:

- cellulose, the main structural component
- hemi-celluloses and pectin
- lignin, the "glue" that gives stiffness and holds the wood matrix together
- extractives, that protect the wood from biological attack.

The proportions of each group of substances varies between wood species and this is further modified by the different pulping processes. The chemistry of mechanical pulps is very similar to that of the parent wood, but the chemistry of chemical pulps will, on the one hand, be somewhat simpler due to removal of a significant proportion of the wood substance, but, on the other hand, somewhat more complex due to the chemical changes wrought on the substances that remain. It is important to note, however, that the four sets of substances present in wood are not distributed uniformly within the tracheid/fibre structures, but each is concentrated in certain parts of the fibre wall:

- the middle lamella is predominantly lignin with hardly any cellulose or hemi-cellulose. Its complete or partial removal during chemical pulping allows the fibres to separate.
- the thin primary wall is about 50% lignin with most of the remainder being hemi-cellulose
- the substantial secondary wall has a low lignin level (averaging about 25% across the 3 layers) with the cellulose reaching its maximum concentration (about 50%) in the thickest S2 layer. The cellulose chains are associated in various types of fibril, which grow at a certain angle to the fibre's long axis. This angle is very important in relation to the pulp's mechanical properties and its hygroexpansivity As the angle increases, strength (tensile and stiffness) is lowered and the greater CD to MD hygro-expansion is reduced.

The actual density of the wood substances is about 1500 kg/m^3, so the actual density of the dry wood (see above) reflects the void structure of the fibres present which is quite different between hardwoods and softwoods.

Wood-containing papers

This term is used to describe those papers in which mechanical pulp is the main fibrous component although this distinction can be difficult to quantify as these grades are increasingly made from at least some recycled pulp. With the exception of the important packaging grade of folding boxboard (which is never classified in this sector, but is largely made from mechanical pulp), the three main wood-containing grades are all used exclusively for printing applications:

- newsprint, which is made from 100% or close to 100% pulp, which is mainly mechanical pulp when made from a virgin pulp, but is increasingly made from 100% recovered papers
- super-calendered (SC) papers, which are made from a combination of mechanical and bleached Kraft pulps with up to 35% mineral filler
- light-weight coated (LWC) papers, which are again made from a combination of mechanical and bleached Kraft pulps, but are coated either off- or on-machine.

In fact, these papers form a family of grades increasing in price/value and “quality” from newsprint grades through SC to LWC grades. At the interface between SC and LWC grades, a number of new grades have been developed during the last 20 years in attempts to make papers for the premium quality LWC market, but without the use of full coating. These grades (eg machine-finished pigmentised [MFP] and machine-finished coated [MFC]) use either a metering size press or short-dwell surface applicator to apply a mixture of starch and coating pigment.

Partly in view of the significant contribution from mechanical and/or deinked pulp to the papermaking furnish, paper machines making wood-containing papers share a number of common characteristics:

- high wet end fines content, particularly for the higher-filled SC grades
- high level of anionic trash from pulps and from coated broke for LWC grades
- acidic wet end pH (5-6) in view of the adverse effect of more neutral pH on pitch problems, drainage and product brightness
- fast machines often with two-sided drainage (gap formers) to give an even-sided product.

This combination of attributes provides a very challenging environment in terms of retention chemistry.

Wood-free papers

This is a very broad category of paper products, the main application of which is for some form of printing. Wood-free papers extend from bulk commodity grades such as copier paper to speciality grades such as carbonless copy paper. They are often referred to just as “fine papers”. The distinguishing feature of all wood-free papers is that the pulp component must contain no more than 10% mechanical pulp in order to be called wood-free (which means free of wood-like mechanical pulp not free of wood-derived pulp of any sort). The pulp may be based on wood or non-wood fibres, but wood fibres are the most common pulp source. Recovered papers are used, albeit not extensively, in the manufacture of such grades, but only after deinking for post-consumer grades. Wood-free papers are used for many printing/writing applications in offices such as letterheads, copying, brochures, etc and in a coated form for premium quality printing applications. Other paper grades (eg tissue and some packagings) may be wood-free, but they are not classified under this heading.

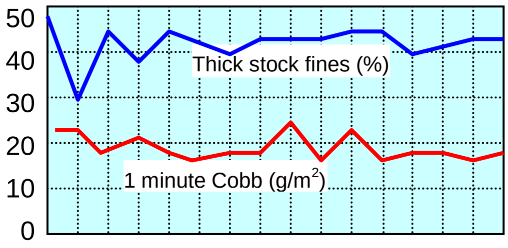
A wood-free paper's non-fibrous components would usually include:

- filler, which is most commonly some form of calcium carbonate, but can be any of the mineral fillers depending on the precise grade being made and the mill location
- a sizing agent, which is most commonly AKD or perhaps its alkenyl version, but can also be ASA or rosin
- a dry strength agent, which is most commonly a combination of wet end-added cationic starch for body strength and another starch (added via some form of surface applicator) for surface strength
- wet strength agents, which are not required for commodity wood-free grades, but are used in specialised grades such as label papers
- fluorescent brighteners for non-coloured grades, which may be added at the wet end and/or by surface application
- dyes for coloured grades, which are nearly always added at the wet end
- coating chemicals (mainly pigment and binder) for coated grades.

As noted at the top of the above list, fillers are always used in these grades and account for 10-30% of the paper’s weight. The last 30 years or so has seen a tremendous change in the type of filler used in wood-free grades, which has seen a move away from kaolin clay in favour of calcium carbonate. This trend started in Europe, where calcium carbonate was abundant at a lower cost and in a brighter form than clay, but has since extended to most papermaking regions. The use of calcium carbonate was made possible by the development of reliable, cost effective wet end sizing agents that worked effectively at neutral pH. The elimination of high alum doses and of the acid wet end pH lead to further benefits such as a stronger, more durable paper and a more stable wet end chemistry within the process. The main economic benefits of this change are the possibilities to replace pulp by filler (due to the higher strength of neutral papers) and to increase machine speeds through the better drainage characteristics of calcium carbonate-filled furnishes.

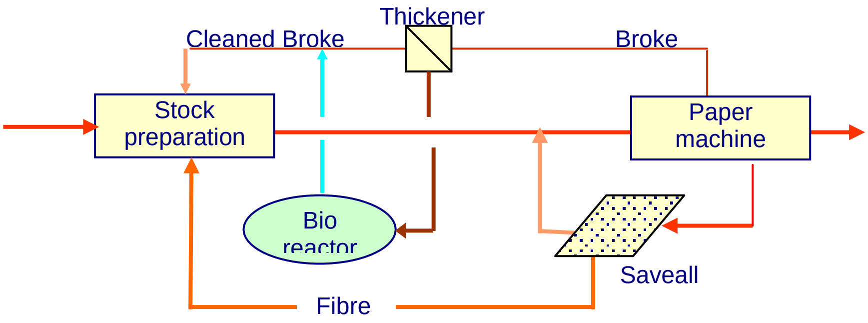
Examples of chemistry data from wood-free paper machines are given elsewhere in this document:

- an example of a clay-filled, rosin-sized machine in terms of the dependence of fines retentions on grammage and their impact on rosin retentions
- an example of variations on a coated wood-free paper machine



A third example is given at right, which relates to the second set of data (shown here) illustrating the effect of grammage on single pass retentions. This machine makes neutral AKD sized paper of fairly low grammage (35-55 g/m^2). The machine conductivity (1.0 to 1.2 mS/cm) is somewhat higher than the fresh water conductivity (0.8 mS/cm) due to electrolytes derived from pulps as no ionic additives were in use. The level of dissolved organics was low (100-200 mg COD/l) and are mainly pulp-derived hemi-celluloses. Both these set of dissolved substances are quite low due to the limited inputs from non-water sources and the quite open water system (30-40 m^3/tonne) on this machine. The variations in thick stock fines shown at right above reflected changes in the balance of bleached hardwood and softwood Kraft pulps and the type of wet end filler used (see here for further data from this study on titanium dioxide retention), but are high throughout the monitoring period. The sizing of the paper was excellent (see figure above) and became very stable during the final period, which coincided with very high single pass retentions (SPR) of the fines fraction. This would be expected if the AKD size is aggregated simply as part of the rest of the particulate matrix (see this figure) and is one of the significant benefits of being able to achieve a high SPR and make paper of acceptable formation quality.

Other than machine retentions, the most important process control issue on wood-free paper machines is the system microbiology. Because of the high visual quality of these papers, slime debris in the paper cannot be tolerated, but the papermaking system represents an ideal environment for microbiological growth due to the high starch use. The most significant contribution to wet end starch levels is not the starch added at the wet end, but the starch dissolved from the size press-treated broke, which can easily generate wet end concentrations measured in 100s of mg/l or even 1000s of mg/l on machines with substantially closed water systems. These levels can only be prevented by using more retentive size press starches (ie cationic starches) or by washing the broke prior to recycling and possibly linking this to some form of integrated bio-treatment of the filtrate (as shown at right) . If fluorescent brighteners make a significant contribution to broke-derived dissolved organics, a different approach to treatment may be required as they are not biodegradable. Both the brighteners and some types of size press starch (eg oxidised starches) would also contribute to anionic trash levels, which provides a further incentive to address this problem at its source.

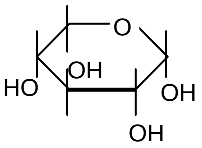


WRV

This abbreviation stands for water retention value.

Xylose

This is one of the five simple sugars that are present in two hemi-celluloses - the arabinoglucuronoxylans and the glucuronoxylans. It is a pentose with the formula $C_5H_{10}O_5$ and the structure shown at right (drawn with a pyranose structure in the α-anomer form - see glucose for explanation of these terms).

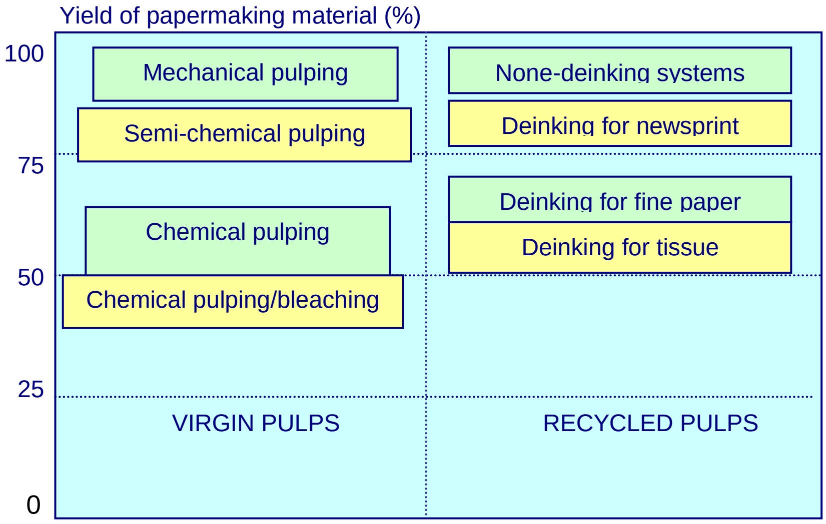


Yankee cylinder

This is the large single cylinder that is used to dry the paper on some tissue and towel machines.

Yield

This term is widely used in pulping, deinking and papermaking to denote the overall efficiency in converting raw materials into product. It is synonymous with the term total retention in papermaking. Yields across pulping/bleaching of virgin fibres and deinking of recovered papers span a similar range as shown in the figure below. Yields for converting the range of papermaking materials into paper products should be above 95% in most cases, the best achievable probably being around 98% unless the water system is fully-closed in which case the yield is close to 100%.



Young equation

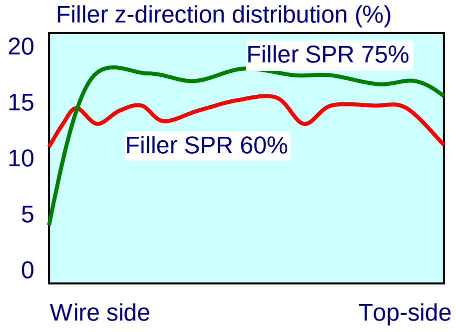
This equation links the three interfacial energies acting between a solid surface, liquid and vapour and is shown under interfacial energy.

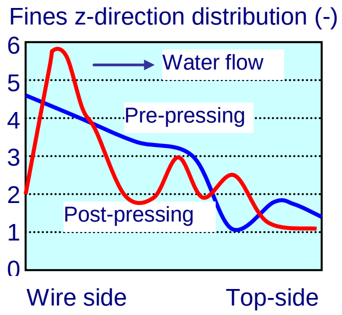
z-direction

This term refers to the depth or thickness axis of the paper sheet, which goes from the bottom or wire side to the top or felt side.

z-distribution

This terms refers to the distribution of materials in the z-direction of the paper. Ideally, all materials should have a similar concentration in each layer of the sheet, but there is an inherent tendency for the level of fine particulate solids to be higher on the top-side. This gives rise to some two-sidedness in the paper. One of the most common causes of an uneven z-distribution is poor aggregation of the fines fraction, which is then retained in the sheet mainly by filtration through the fibrous mat rather than by hetero-aggregation with the rest of the particulate matrix. The figure at right illustrates this effect for filler distribution and clearly shows one of the many benefits of high single pass retention. Another example is shown here for an SC paper machine.





Source: Cutshall in Tappi J., 1990, 73, 6, 81-90.

However, the distribution of fines is not fixed after the paper web reaches the couch roll as some materials can follow the water flow during pressing. The example at left shows the variation in fines content through pressing, where the top side is in contact with the press fabric. This particular paper has an unusual pre-press fines distribution in that the wire-side is rich in fines, but pressing transports some of this material into the sheet, thus giving a more uniform fines distribution.

Zeta potential

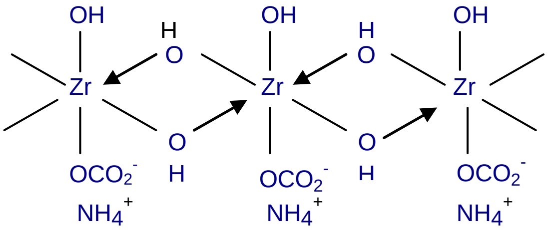
This is the potential at the plane of shear within the electrical double layer that surrounds all charged particles. It can be measured by any of the four electrokinetic methods, but the two used in practice are electrophoresis and streaming potential. Examples of the zeta potential of various papermaking materials are given here for the effect of pH on bleached Kraft pulp, here for the effect of alum on pulp, here for the various furnishes on a folding boxboard machine and here for the effect of pH on the charge of AKD sizes.

However, there have been several other approaches to zeta potential measurement:

- ❑ the Electrophoretic Mass Transport Analyser was used by several researchers in the 1970s, but gave poor correlation with results from conventional electrophoresis and has thus been little used since. The technique was developed for concentrated mineral suspensions and measures the mass of material transferred between two containers due to an applied voltage maintained for several minutes.

- ❑ if a colloidal sample is exposed to ultrasound, the electrical double layer is shifted more than the particle itself. This differential movement generates an alternating voltage with a frequency dependent on the ultrasound pressure (the Debye effect). This technique was available in an instrument from Pen-Kem in the USA.
- ❑ when a high frequency electric field is applied to the sample, the particles move electrophoretically and, if there is a density difference between the particle and the liquid, this motion generates an alternating acoustic wave. This method has the advantage that it can be applied to samples at high concentration with no need for sample dilution and the resultant matrix changes. This technique is patented as the electrokinetic sonic amplitude method with a commercial instrument available from Matec in the USA.

Zirconium compounds



Zirconium is in Group 4 of the Periodic Table and is one of the few transition metals that features in papermaking chemicals. Their main application is as insolubilisers in size press solutions and coating formulations, the most common salt being ammonium zirconium (or zirconyl) carbonate (AZC). The zirconium ion has a valency of +4 and has a strong tendency to form bonds with oxygen-containing species. The formula of AZC as a solid is $(NH_4)_2ZrO(CO_3)_2$, but it is normally supplied as an alkaline solution containing about 20% zirconium as ZrO_2. As seen above, AZC in solution has the structure of a zirconium polymer connected by hydroxo bridges (as in the olated polymers formed by alum in acid solution) with terminal hydroxyl groups at the chain ends. Commercial solutions usually contain excess carbonate ions for stability and to control the polymer size.

AZC has two types of interaction with substances present at the size press or coater:

- ❑ with hydroxyl groups via hydrogen bonds with its own hydroxyl groups. This weak interaction occurs with starches, CMC and PVOH and clays, leading to rheological changes, notably at low shear.
- ❑ with carboxyl groups on other substances (latices, proteins, calcium carbonate) by displacing the attached carbonate ions. This reaction occurs when the paper is being dried so does not produce any rheological changes during coating, provided that the pH is kept alkaline.

Both these interactions cause cross-linking of the co-reactant, which then affects other properties of the surface film/coating such as water retention, migration and hold-out. There may also be other upstream benefits when the surface-treated broke is recycled in terms of reduce dissolution and deposition.

LIST OF ENTRIES

Abietic acids
Absorbency
Absorption
Accessibility
Acetic acid
Acid
Acidity
Acid papermaking
Acid dye
Acrylates
Activity
Adhesion
Adipic acid
Adsorbable organohalogens
Adsorption
Aerobic
Affinity
Aggregation
AKD
Alcohols
Aldehydes
Alginates
Alkali
Alkalinity
Alkaline papermaking
Alkenyl ketene dimer
Alkenyl succinic anhydride
Alkyl ketene dimer
Alum
Aluminium compounds
Aluminium hydroxide
Aluminium nitrate
Aluminium oxide (alumina)
Aluminium oxyhydroxide
Aluminium sulphate
Aluminosilicates
Amides
Amines
Amino acids
Ammonia
Ammonium bromide
Ammonium persulphate
Amphipathic
Amphoteric
Amphoteric starch
Amylases
Amylopectin
Amylose
Anaerobic
Analytical techniques
Angstrom
Anhydroglucose
Anions
Anionic
Anionic demand
Anionic dyes
Anionic polymers
Anionic starch
Anionic trash
Anisometric
Anisotropic
Anomer
Antifoam
Anti-scalant
Anthraquinone
AOX
Arabinoglucuronoxylans
Arabinose
ASA
Ash
Aspect ratio
Atom
ATC
Attractive forces
Auxochromes
Azo compounds
Bacteria
Bacteria in papermaking
Bag papers
Barrier coatings
Barium compounds
Base
Baseline chemistry
Basicity
Basic dyes
Bauer-McNett classification
BCDMH
Beating
Bentonite
Bicarbonate
Binder
Biochemical oxygen demand
Biocide
Biodegradability
Biofilm inhibition
Biological treatment
Biotechnology
Birch
BK
Blanc Fixe
Bleached chemical pulps
Bleached Kraft (sulphate) pulps
Bleached mechanical pulps
Bleached sulphite pulps
Bleaching
Board
BOD
Bond
Borate
Bridging
Brightener
Brightness
Brightness reversion
Britt Jar
Broke
Bromine
Brownian motion
Bulk
Burst strength
Butyric acid
Calcined clay
Calcium
Calcium bicarbonate
Calcium carbonate
Calcium oxalate
Calcium stearate
Calcium sulphate
Calendering
Caliper
Canadian Standard Freeness
Carbohydrate
Carbon
Carbonate
Carbon dioxide
Carbonless-copy paper
Carbonyl
Carboxylic acids
Carboxymethylcellulose
Casein
Catalase
Cation
Cationic
Cationic demand
Cationic dye
Cationic polymer
Cationic starch
Caustic soda
Cellobiose
Cellulases
Cellulose
CFU
Chalk
Charge
Charge demand
Charge density
Charge interactions
Charge neutralisation
Charge titration
Chelant
Chemical bonds
Chemical pulps
Chemical oxygen demand
Chemimechanical pulps
Chemistry
Chitosan
Chloramines
Chloride
Chlorinated paraffins
Chlorine
Chlorine dioxide
Chloroform
CHPT
Chromium compounds
Chromogen
Chromophores
CIE
Clay
Closing up
CMC
Coagulation
Coarseness
Coated papers
Coating
Cobb value
Cockle
COD
Colloidal silica
Colloid chemistry
Colloid protection
Colloid titration
Colorants
Colour

Insolubilisers
Intensive
Interfacial energy/tension
Interfering substances
Internal sizing
Ionenes
Ion exchange
Ionic bonds
Ionic strength
Ions
Isoelectric point
Isomers
Joule
K
Kaolin clay
Kappa number
Ketones
Kinetics
Kraft pulps
Kubelka-Munk Theory
Lactic acid
Lactones
Langelier's equation
Latency
Latex
Light absorption
Light scattering
Light-weight coated paper
Lignan
Lignin
Lignosulphonates
Lime
Limestone
Linerboard
Linting
Lipophile
Liquid packagings
Locust bean gum
Lubricants
Lumen
LWC
Magnesium
Maize starches
Maleic anhydride
Maltose
Mannose
Marble
Mass
Mechanical pulps
Melamine-formaldehyde resins
Metamerism
MG
Micelle
Microbiological chemistry
Microbiology
Micro-organisms
Microbiological problems
Micro-particles
Middle lamella
Minerals
Modelling
Molarity
Mole
Molecular mass/weight
Monodisperse
Monosaccharide
Montmorillinite
Mottle
Nano-particles
Natural papermaking
Neutral papermaking
Neutral sulphite semichem pulp
Neutron
Newsprint
Newton
Nitrate
Nitrogen
NMR
Non-deinked pulps
Non-fibrous raw materials
Nonionic
Non-wood pulps
NSSC
Nucleophilic
OBA
Odours
Olation
Oligosaccharide
On-line monitoring
Opacity
Optical brightener
Optical properties of paper
Organic acids
Organic chemistry
Organo-bromine compounds
Organo-chlorine compounds
Organo-fluorine compounds
Organo-halogen compounds
Organo-nitrogen compounds
Organo-phosphorous compounds
Organo-silicon compounds
Organo-sulphur compounds
Orthokinetic
Osmotic pressure
Oxidation
Oxidised starch
Oxidising agents
Oxidising biocides
Oxalic acid
Oxolation
Oxygen
Ozone
p
PAC
Packaging papers/boards
Paper chemistry
Papermaking
Paper microbiology
Paper products
Paper properties
Paper quality
Parenchyma cells
Particle aggregation
Particle characteristics
Particle charge
Particle size
PASS
Patch flocculation
PCBs
PCC
PCP
Pectin
PEI
Pentachlorophenol
Pentose
PEO
Peracetic acid
Perikinetic
Periodic Table
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