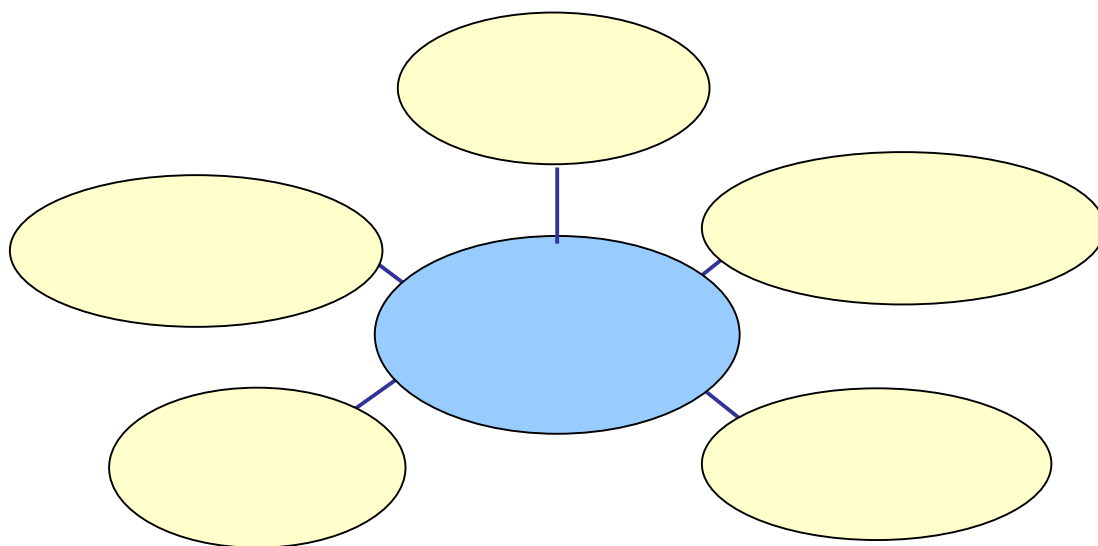


A-Z OF PRACTICAL PAPER CHEMISTRY
DEMONSTRATION VERSION



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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" view and it is recommended that the document is not viewed in "online layout" view as this changes the position of drawings/figures so that they are no longer in the best place. Within "page layout" view, 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.

On this demonstration version, most of the text is omitted, but there are several full entries so that you can get an idea of the technical content and level. These entries are highlighted by being in **UPPER CASE** in the document map (excluding abbreviations).

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.

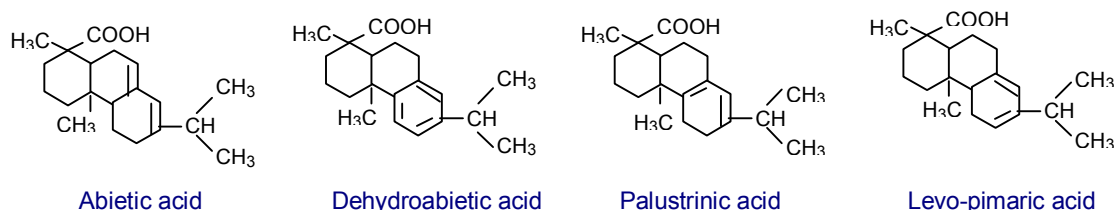
[Raw materials](#) is a useful starting point if you wish to explore the general sorts of substances that go into paper products from the view[point of their functionality.

Acknowledgements

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

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:



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°C.

Absorbency

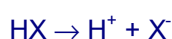
Absorption

Accessibility

Acetic acid

ACID

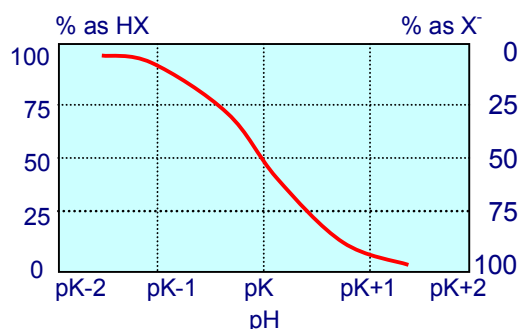
In contrast to a [base](#), an acid is a [proton](#) donor through its ionisation reaction:



the equilibrium constant, $K_A = c_{H^+} \cdot c_{X^-} / c_{HX}$ 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 :



The pK_A value is about 2 for ionisation of its first proton, but the second proton ionises at a much higher pH ($\text{pK}_A = 7$) 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 ($\text{pK}_A = 13$) 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

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

Acrylates

Activity

Adhesion

Adipic acid

Adsorbable organohalogens

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:

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

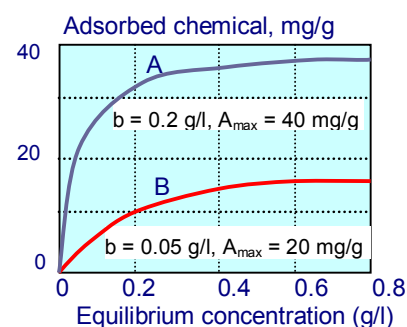
where A = adsorbed quantity of substance (adsorbate) per unit mass of adsorbent

A_{\max} = maximum quantity adsorbed per unit mass of adsorbent

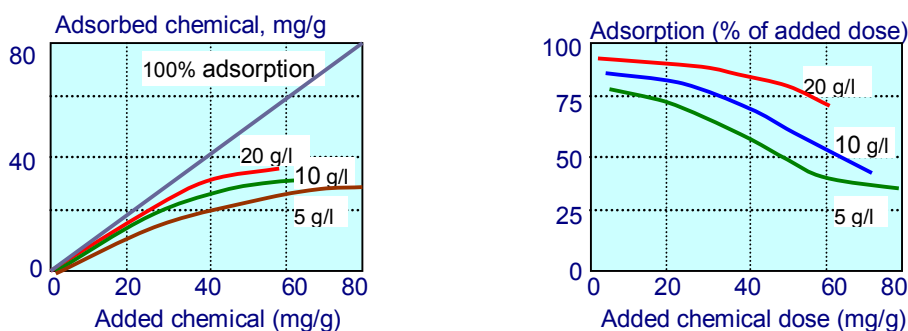
c = equilibrium concentration of substance remaining in solution

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).

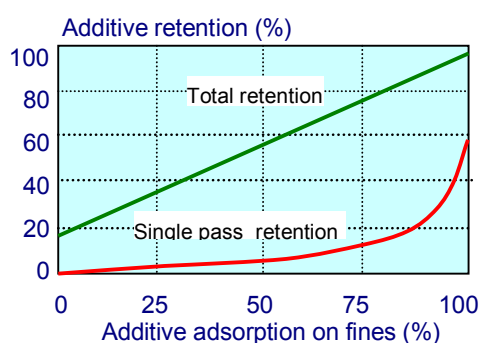


In some cases, it is useful to look at adsorption in terms of the adsorbed quantity versus the amount of substance added and this calculation also involves the concentration of the adsorbate. This can be plotted in two forms - the adsorbed quantity versus the dose at different adsorbent levels (as shown 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.

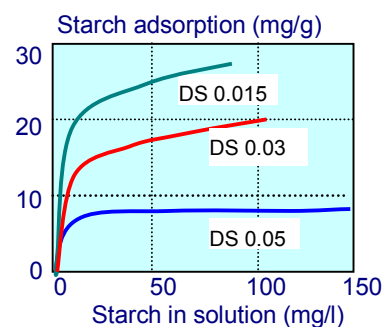
The retention of a water-soluble wet end additive is critically dependent on its adsorption on the particulate matrix, as illustrated in the figure at right below using the standard [model](#) of the papermaking wet end. This example assumes that the additive adsorbs only on the [fines](#) fraction, 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 m³/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.

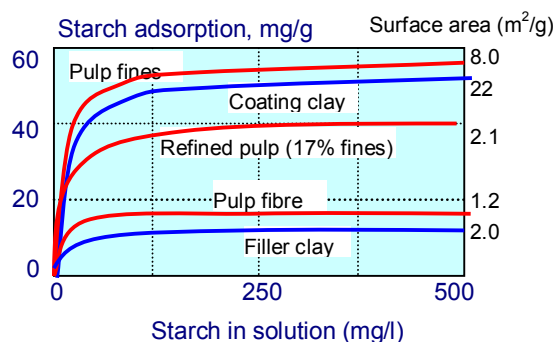


Source: Wagberg, Nordic Pulp Paper Research J., 1993, 4, 399-404.

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 limit 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**

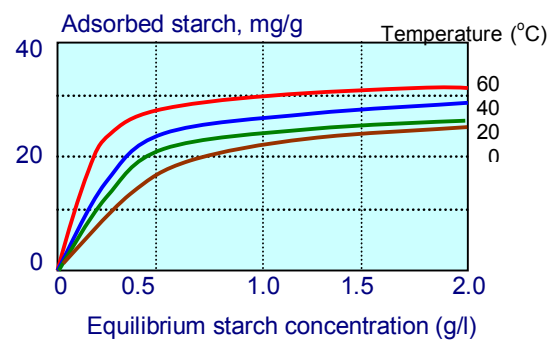
The surface area of the adsorbent depends mainly on its [particle size](#), but also on its [shape](#), there being an order of magnitude difference in the specific surface area of the larger particles (intact fibres) and [fines](#) (see this [table](#)). For fibre surfaces, adsorption also depends on 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



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

hardwood-softwood bleached Kraft pulp and for two different clays.

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

Affinity

Aggregation

AKD

Alcohols

Alginates

Alkali

Alkalinity

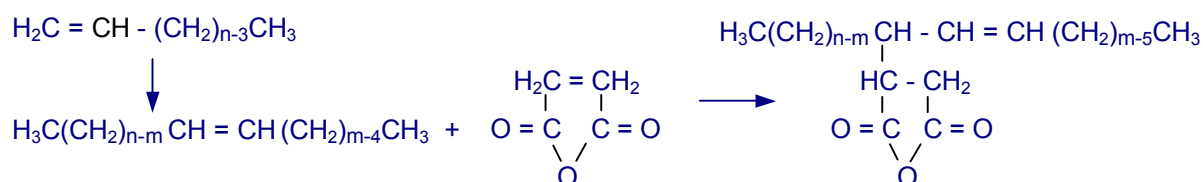
Alkaline papermaking

Alkenyl ketene dimer

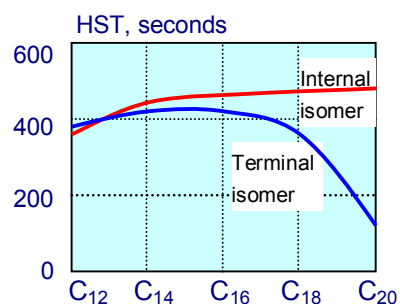
ALKENYL SUCCINIC ANHYDRIDE (ASA)

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:



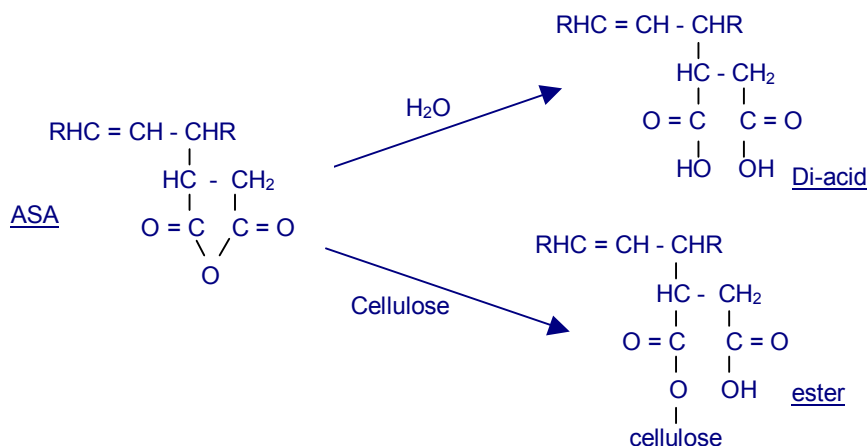
The name [succinic](#) anhydride comes from the name for hydrogenated maleic anhydride (no alkene linkage), which is the form in the ASA molecule. The total length of the alkenyl chain (n in the above reactions) is in the range 15 to 20, the most common chain length in commercial products being 16 and 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](#)).



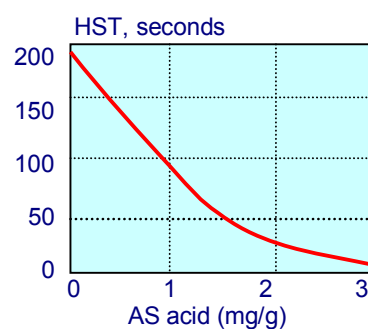
Source: Roberts at Pira Conference "Chemistry of Papermaking", 1993.

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 (C₁₈) 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 C₁₈ 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.



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.



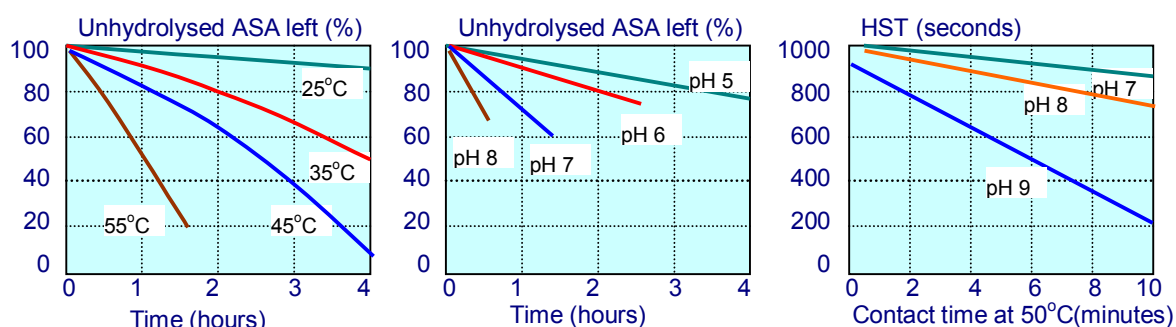
Source: Roberts in Proceedings 10TH Cellulose Conference, Syracuse, 1988.

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

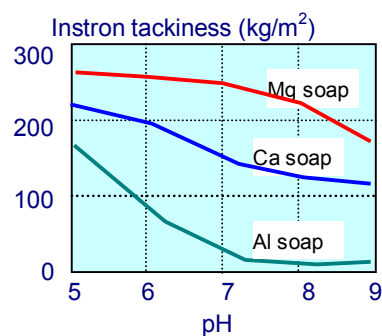
released from its emulsification role. Whilst little effect of starch molecular weight has been observed in relation to ASA sizing performance, this would be still important in relation to its dry strengthening.

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.

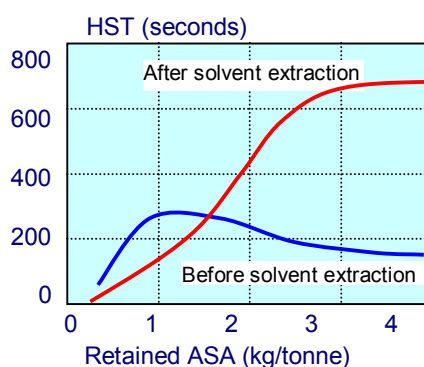
The di-acid hydrolysis product can react with any cations available to form the soap, [calcium](#) being the most prevalent ion in most papermaking systems that use ASA size at neutral pH. As shown in the figure at right, the calcium soap is quite tacky (although less so than the [magnesium](#) soap), 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 slippery 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.



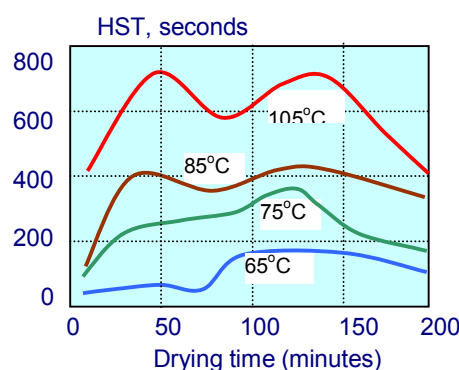
Source: Proverb in Proceedings 1989 Tappi Papermakers Conference, 91-96.

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).

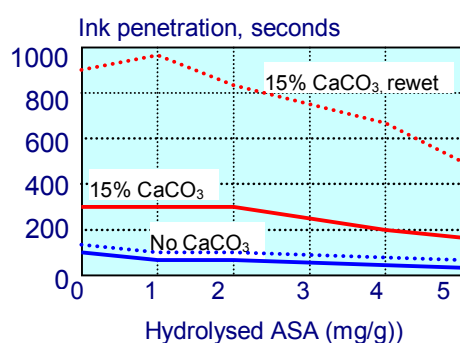


Source: Roberts in Proceedings 10TH Cellulose Conference, Syracuse, 1988.



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 slippery 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)

Alum

Aluminium compounds

Aluminium hydroxide

Aluminium nitrate

Aluminium oxide (alumina)

Aluminium oxyhydroxide

Aluminium sulphate

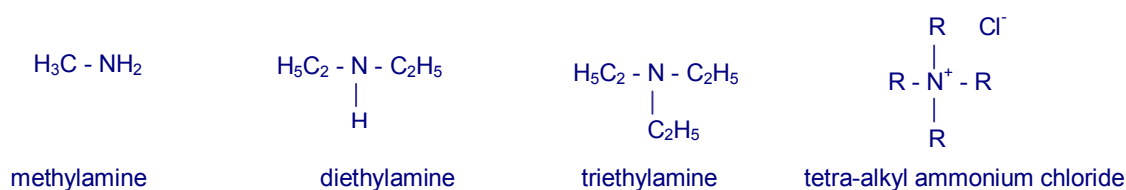
Aluminosilicates

Amides

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).



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 ($\text{CH}_3\text{NH}_3\text{Cl}$). 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

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 (AQ)

AOX

Arabinoglucuronoxylans

Arabinose

ASA

Ash

Aspect ratio

Atom

ATC

Attractive forces

Auxochromes

Azo compounds

Bacteria

Bacteria in papermaking

Bag papers

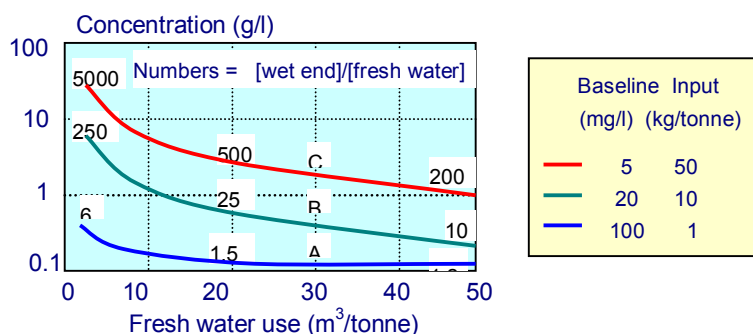
Barrier coatings

Barium compounds

Base

BASELINE CHEMISTRY

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

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

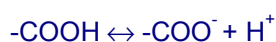
Carbonyl

CARBOXYLIC ACIDS

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.



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)

Casein

Catalase

Cation

Cationic

Cationic demand

Cationic dye

Cationic polymer

Cationic starch

Caustic soda

Cellobiose

Cellulases

Cellulose

CFU

Chalk

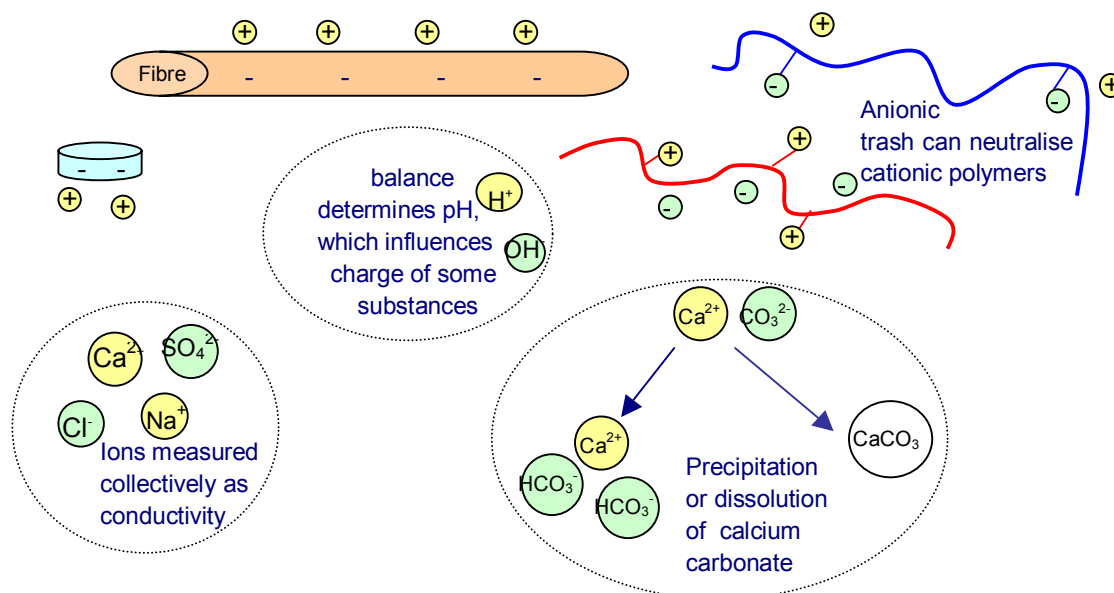
Charge

Charge density

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

Charge titration

Chelant

Chemical bonds

Chemical pulps

Chemical oxygen demand (COD)

Chemimechanical pulps

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

Conductivity

Conformation

Consistency

Contact angle

Conversion

Co-ordinate bond

Copper

Corn starches

Corrosion

Corrugated cases

Corrugating medium

Covalent bond

Creping

Crowding number

CSF

CTMP

Curing

Curl

Cyanates

Dalton

DBNPA

DCP

DCS

DDJ

Deaeration

Debonder

Deflaking

Defoamer

Degassing

Degradation

Degree of polymerisation

Degree of substitution

Deinked pulp

Dendrimer

Density

Deposition

Deposits

Desorption

Dewatering

Dichloropropanol (DCP)

Dicyandiamide

Dielectric constant

Diffusion

Di-isopropyl-naphthalene

Dimensional properties of paper

Dioxins

DIPN

Dipole moment

Direct dye

Disinfection

Dispersant

Dispersion

Dissolution

Dissolved organic carbon

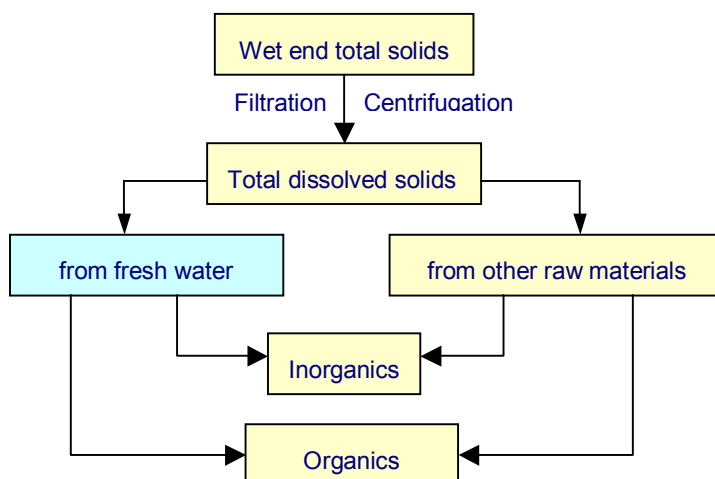
Dissolved organics

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 colloiddally-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

DOC

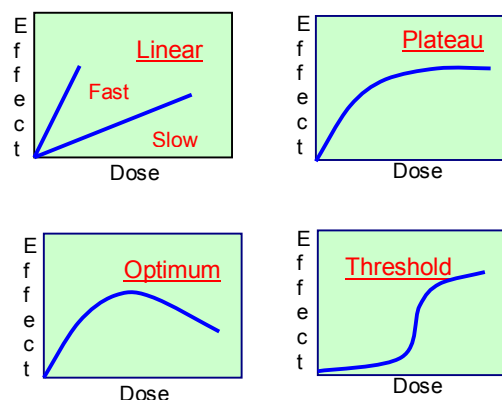
Donnan effect

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

DP

Drainage

Drainage aids

Dry end chemistry

Drying

Dry strength agent

DS

DTPA

Dyes

Dynamic drainage jar (DDJ)

ECF

EDTA

Efflux ratio

Electrical double layer

Electrochemical treatment

Electrochemistry

Electrokinetics

Electrolytes

Electron

Electrophilic

Electrophoresis

Electrostatic forces

Elemental chlorine free (ECF) pulps

Emulsion

Energy

Enthalpy

Entrained gases

Entropy

Environmental aspects

Enzyme-converted starches

Enzymes

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:

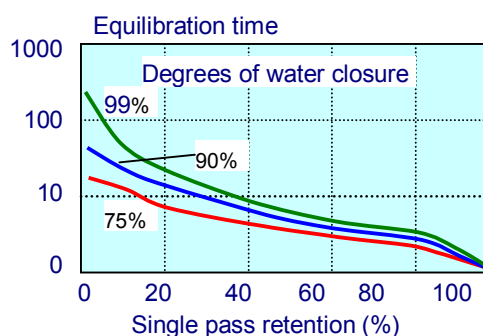
$$\text{Time taken to get to within } X\% \text{ of equilibrium value} = \log(1-X)/\log(f \cdot [1-r])$$

where X = proportion of equilibrium value to be calculated (fraction)

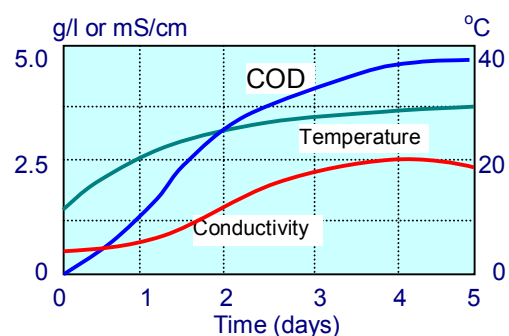
f = [degree of closure](#) (fraction) and r = [single pass retention](#) (fraction)

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 m³/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:



$$\text{Equilibrium constant, } K = \frac{[A][B]}{[C][D]}$$

where [X] represents concentration or [activity](#) of X

All equilibrium constants (K) vary with temperature (T) as follows:

$$\ln K = -\Delta G^\circ/RT = -\Delta H^\circ/RT + \Delta S^\circ/R$$

$$\text{which on integration, } \ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

where G° = Gibb's [free energy](#) under standard conditions

H° = [enthalpy](#) and S° = [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

Ester

Ethers

Ethylene vinyl acetate (EVA)

Eucalypts

Extensive

Extractives

FAS

Fastness

Fatty acids

FBA

Fermentation

Fibre

Fibrils

Fillers

Film formation

Filtration

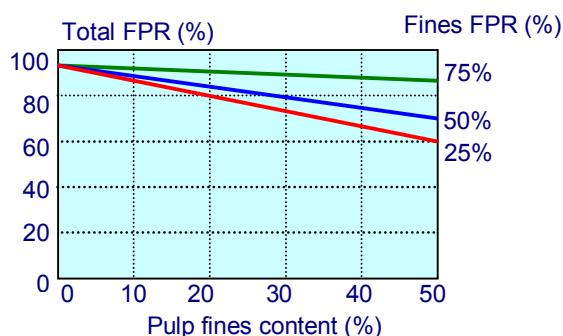
Fines

FIRST PASS RETENTION

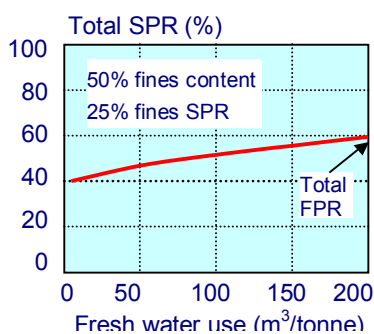
This term is often used interchangeably with [single pass retention](#), but it is best used explicitly to refer to the single pass retention under start-up conditions, ie the very first time that the furnish passes the flowbox. At actual start-up, the composition of the thin stock at the flowbox is 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:

$$\text{Total FPR} = (\text{Pulp fibre content} \times \text{fibre FPR}) + (\text{Pulp fines content} \times \text{fines FPR})$$

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 m³/tonne), but the total SPR under conditions of high water closure (about 4m³/tonne) is about 40%. The equilibrium SPR is always lower than the start-up FPR due to the fines build-up.

Fixative

Flocculation

Floc strength

Fluorescent brightening agents

Fluorescent whitening agents

Fluorine

Fluting

Foam

Folding boxboard

Folding endurance

Force

Formadine-sulphinic acid (FAS)

Formaldehyde

Formation

Formation aids

Fortified rosin

FPR

Free energy

Freeness

Friction

Fresh water

Fugitive sizing

Fungi

Furans

Furnish

FWA

Galactose

Galactoglucomannan

Galactomannans

Galacturonic acid

Gases

GCC

Gelatin

Glassine

Glass transition temperature

Glucomannans

Glucose

Glucuronic acid

Glucuronoxylan

Gluteraldehyde

Glycerol

Glycols

Glyoxal

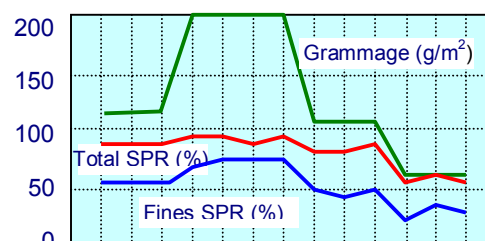
Glyoxalated polyacrylamides

GRAMMAGE

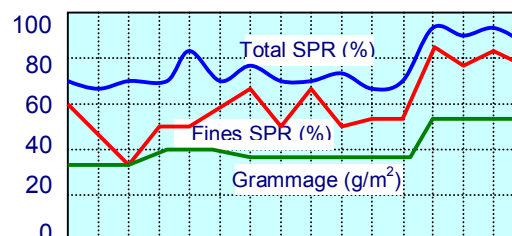
This is the term for the areal [mass](#) of the paper, which is sometimes referred to as its basis weight and is most commonly expressed in units of g/m^2 . In North America, the grammage of boards can be expressed in pounds per 1000 feet² where 100 g/m^2 is 20.5 pounds per 1000 feet². The grammage of 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

Groundwood pulps

Guanidine

Guar gum

Gum arabic

Gums

Gypsum

Halogens

Hardness

Hardwood

Hectorite

Hemi-celluloses

Henry's Law

Hercules size test

Hexenuronic acids

Hexose

HLB

Hornification

HST

Humectants

Hydantoins

Hydrocarbons

Hydrocolloids

Hydrogen

Hydrogen bonds

Hydrogen peroxide

Hydrogen sulphide

Hydrolysate

Hydrolysis

Hydrophile-lipophile balance (HLB)

Hydrophilic

Hydrophobic

Hydroxyl

Hydroxonium

Hypobromous acid

Hypochlorous acid

Inks

Inorganic chemistry

Insolubilisers

Intensive

Interfacial energy/tension

Interfering substances

Internal sizing

Ionenes

Ion exchange

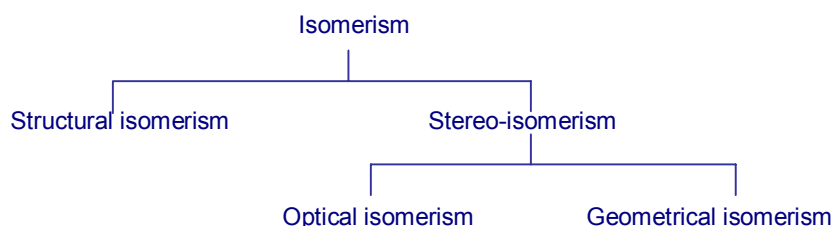
Ionic bonds

Ionic strength

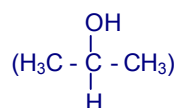
Ions

Isoelectric point

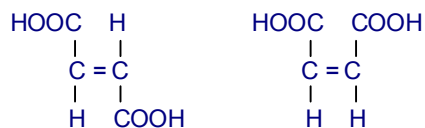
ISOMERS



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 [ethers](#) ($H_3C - O - CH_3$, dimethyl ether), which are very different chemically.



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.



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

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 (MF) 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

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

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

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 the -CONH₂
- ❑ [amines](#), which are compounds containing the -NH₂ 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(H₂O)_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-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

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.
- ❑ 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).

$\text{pH} = -\log[\text{H}^+]$ where $[\text{H}^+]$ is measured as [molarity](#) or, more strictly, as [activity](#).

An alternative way of looking at this is: $[\text{H}^+] = 10^{-\text{pH}}$

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:

$$K_w = [\text{H}^+][\text{OH}^-]$$

At 25°C, $K_w = 1 \times 10^{-14}$, ie $\text{p}K_w = 14$ and $\text{pH} = \text{pOH} = 7$.

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°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

Phosphates

Phosphonate

Physical chemistry

Picking

Pigment

Pimaric acid

Pine

Pitch

pK value

Plasterboard

Plastic pigments

Poise

Polyacrylamides

Polyacrylates

Polyaluminium chlorides (PAC)

Polyaluminium silico-sulphate

Polyaminoamide-epichlorhydrin (PAE) resins

Polyamines

Polychlorinatedbiphenyls (PCBs)

Polyelectrolyte

Polyethylene

Polyethyleneglycol

Polyethyleneimine (PEI)

Polyethyleneoxide (PEO)

Polyisocyanates

Polymers

Polypropyleneglycol

Polysaccharides

Polyurethanes

Polyvinyl alcohol (PVOH)

Polyvinylamines

Polvinylpyrrolidone

Porosity

Potassium

Potassium monopersulphate

Potato starches

Potential

ppmv

Precipitation

Precipitated calcium carbonate (PCC)

Preservatives

Pressing

Printing

Printing papers

Problematic substances

Propionic acid

Proteins

Proton

Pulps

PVA

PVAc

PVOH

Quaternary ammonium compounds

Quaternary nitrogen compounds

Quenching

Radius of gyration

Raw materials

Reaction chemistry

Recovered paper

Recyclability

Recycled pulps

Recycled water

Redox potential

Reduction

Refiner mechanical pulp (RMP)

Refining

Reflectance

Reflocculation

Refractive index

Release agent

Repulsive forces

Resin acids

Resistivity

Retention

Retrogradation

Reversion

Rheology

RMP

Rosin

Roughness

Runnability

Sack papers

Salts

Sampling

Saponify

Satin white

Saveall

SB

SC

Scale

SCD

Schopper-Riegler (SR)

Schulze-Hardy Rule

Self-sizing

Sensitisation

Sequestrant

SGW

Shear

Shives

Silicon

Silica

Silicates

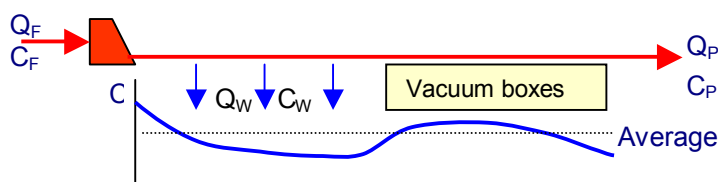
Silicones

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



$$\begin{aligned}
 \text{Single pass retention} &= M_P/M_F = Q_P \cdot C_P / Q_F \cdot C_F \\
 &= (Q_F \cdot C_F - Q_W \cdot C_W) / Q_F \cdot C_F \\
 &= 1 - (Q_W \cdot C_W / Q_F \cdot C_F) \\
 &= 1 - (C_W / C_F) \text{ as } Q_W \sim Q_F
 \end{aligned}$$

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 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%)**

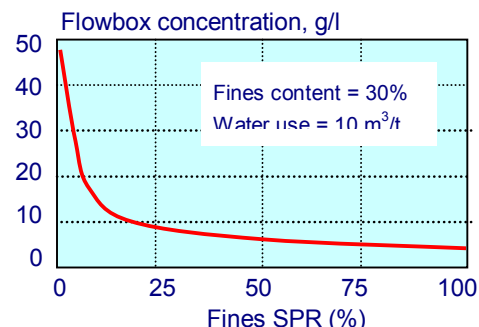
This covers a wide range of particulate materials extending downwards in [particle size](#) from pulp [fines](#) (ie those passing through 200 mesh wire) into the colloidal size range and including, where present, [fillers](#) and [size](#) emulsions. The [natural](#) SPR of this group of materials is 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

Size press

Size reversion

Sizing

Sizing agent, surface

Sizing agents, wet end

Slime

Slip

SMA

Smoothness

Soap

Soda

Soda ash

Soda pulp

Sodium

Sodium aluminate

Sodium bicarbonate

Sodium bromide

Sodium carbonate

Sodium chloride

Sodium dithionite

Sodium hydrosulphite

Sodium hydroxide

Sodium hypobromite

Sodium hypochlorite

Sodium silicate

Sodium sulphate

Sodium sulphite

Softener

Softness

Softwood

Solubility

Solute

Solute exclusion

Solution

Solvent

Sorbitol

Sorption

Specific heat

SPR

Spraying

Spreading

Spruce

Squareness

SR

SRB

Starch, coating

Starch ethers

Starch, general

Starch, wet end

Starch, size press

Steric stabilisation

Stickies

Stiffness

Stoichiometry

Strain

Streaming current

Streaming potential

Strength

Stress

Styrene

Styrene-acrylate ester (SAE) co-polymers

Styrene-acrylic acid (SAA) sizes

Styrene-butadiene (SB) latex

Styrene-maleic anhydride (SMA) sizes

Substantivity

Sugar

Sulphate

Sulphate pulps

Sulphate reduction

Sulphide

Sulphite

Sulphite pulps

Sulphonates

Sulphur

Sulphuric acid

Super-calendered paper

Surface application

Surface energy/tension

Surface properties of paper

Surface strength

Surfactant

Swelling

Symplex

Synthetic pulps

Talc

Tapioca starches

TCF

Tear strength

Temperature

Temporary hardness

Tensile strength

Terpenoids

Tertiary nitrogen

Test liner

Thermally-modified starches

Thermo-chemical starches

Thermodynamics

Thermomechanical pulp (TMP)

Thickening

Thiosulphate

Thixotropic

Tinctorial value

Tissues

Titanium dioxide

TMP

TOC

Totally-chlorine free (TCF) pulps

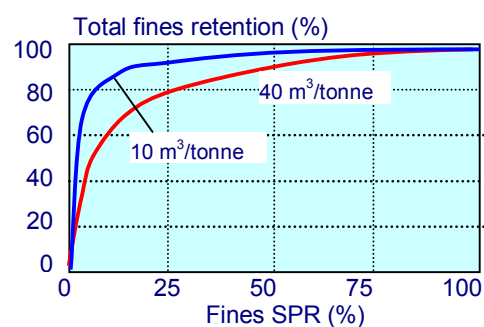
TOTAL RETENTION

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:

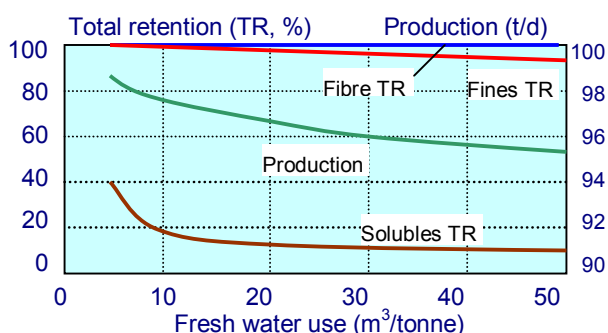
$$\text{Total retention} = \text{SPR} / [1 - X(1 - \text{SPR})] \quad \text{where } X = \text{degree of closure of water circuit}$$

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.

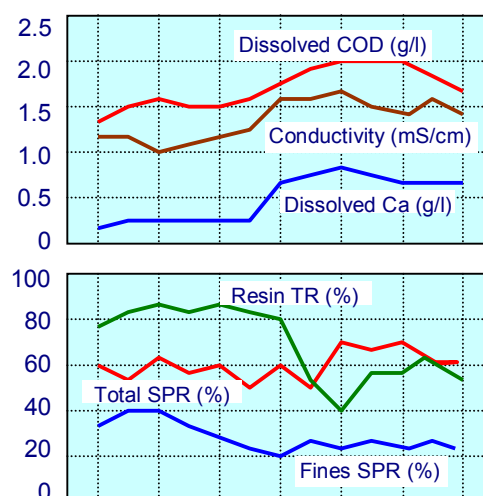
TOWELS

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/m² 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

Turbidity

Two-sidedness

UBK

UF resin

Unbleached chemical pulps

Unbleached Kraft pulps

Uniformity

Urea

Urea-formaldehyde pigments

Urea-formaldehyde (UF) resins

Valency

Van der Waals forces

Vegetable parchment

Velocity gradient

VFA

Virgin pulps

Visco-elasticity

Viscosity

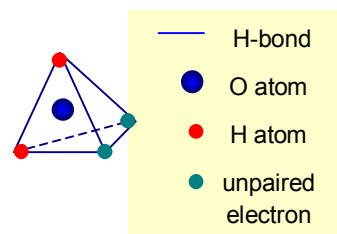
Void volume

Washing

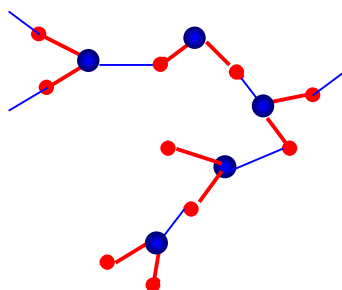
WATER

Water (H₂O) 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 [sp³ 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 H₂O molecules, but several H₂O 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/m² 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](#) (6×10^{-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](#) the papermaking system.

[Water closure](#)

[Water disinfection](#)

[Water retention](#)

[Water retention agent](#)

[Water retention value \(WRV\)](#)

[Waxes](#)

[Wet end additives](#)

[Wet end chemistry](#)

[Wet end interactions](#)

[Wetness](#)

[Wet strength](#)

[Wet strength agents](#)

[Wetting](#)

[Wet web strength](#)

[Wheat starches](#)

[Whiteness](#)

[White pitch](#)

[Wood](#)

[Wood-containing papers](#)

[Wood-free papers](#)

[WRV](#)

[Xylose](#)

[Yankee cylinder](#)

[Yield](#)

[Young equation](#)

[z-direction](#)

[z-distribution](#)

[Zeta potential](#)

[Zirconium compounds](#)