

IPPTA Seminar and Workshops on “Wet End Chemistry with special emphasis on Neutral sizing/Alkaline Sizing”

Keynote Address

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History

The history of paper makingⁱ goes back over 2000 years. Ts'ai Lun, an official of the Chinese Imperial Court, made the first official report on the manufacture of paper in AD 105, although samples of similar materials dating from up to 200 years earlier have been found in the country.

Because of its unique properties and value, the process for manufacturing paper was kept a closely guarded secret within China. The knowledge finally spread westward, along the silk and trade routes, reaching India around 645 A.D.

As we know, a sheet of paper composed only of cellulosic fibres ("waterleaf") is water absorbent. Hence, water-based inks and other aqueous liquids will penetrate and spread in it. Even in the early days of paper manufacture, a method to improve the sheet properties to allow scribes to write clearly was needed. This led to the first sizing techniques to be developed in China in the 8th century, which rapidly spread to India and across the Arab world. The Chinese applied a layer of gypsum and later an adhesive like substance made from lichen to the surface of their paper. Later in the century they made a size from flour starch which was added to the paper pulp in the tub or to the finished sheet after forming.

In an 11th century treatise from an Arabic sourceⁱⁱ, *The writing Base of Scribes and the Instruments of Their Intelligence*, the author describes the process of sizing that prepared the rough sheet for burnishing. In the two translations of this work, the materials used to make the size are variously described as combinations of wheat starch and wheat flour or equal parts of chalk and starch. These were mixed separately in cold water, poured together into boiling water, and stirred until thickened. This thick adhesive-like substance was spread by hand over the sheet of paper in several applications to fill in holes and even out surface irregularities. Then the paper was hung up to dry.

The story of sizing then jumps to Europe, where gelatin was first used to size paper in an Italian mill in Fabriano, in the mid 13th Century. Gelatin is a form of protein based size derived from animal hides, horns, hooves, and bones.

It is not known why gelatin sizing was introduced. Whatever the reason, its use gave the paper a hard, opaque surface that was impervious to the contemporary inks and was well suited to quill pens, qualities which may have helped foster the wide use of paper over parchment. Gelatin sizing spread

across Europe, and was in common use across the continent by the 16th Century.

One of the major problems encountered with gelatin size was that it deteriorated quickly, especially when the weather was hot. In a practice that began in the 16th century and was widely used by the mid 17th century, papermakers added potassium aluminium sulphate (alum) to the size to control the growth of mould and bacteria. There have been estimates that as much as 40% alum was added to the sizing tub. Two other reasons given for the use of alum are that it stabilized the viscosity of the size at various concentrations and temperatures, and increased the ability of a gelatin sized sheet to resist ink penetration.

The two major alum varieties employed in papermaking have not always been distinguished for their different properties. Aluminium potassium sulphate was used until the 19th century. It was then replaced by the newly developed aluminium sulphate, a cheaper and more concentrated source of aluminium compounds.

In 1800 Moritz Friedrich Illig in Germany discovered that paper could be sized in vats with rosin and alum. Although Illig published his discovery in 1807, the method did not come into widespread use for another 25 years. As the use of rosin alum sizing grew, papermakers learned its correct application by trial and error methods. The first valid theory explaining the principles of rosin sizing was not put forward until 1879.

To precipitate one part rosin onto the paper fibres, 1.5 parts alum were required in the pulp solution, but an excess of alum was frequently added to ensure sufficient sizing. Not all of the alum was retained by the paper and some mills recovered it from the white water drained from the wire of the paper machine. Papers which needed to be particularly strong could be sized twice--either with rosin and a subsequent gelatin size or with two gelatin size applications. In such cases, the alum concentration was sometimes increased in the second size bath.

The study of history reveals the use of fillers as early as the 16th century. Interestingly enough, these appear to have been lime or calcium carbonate minerals – possibly left over from pulping practices. These had the added benefit of crosslinking the gelatin size, making it insoluble – and as a consequence less hospitable to micro-organisms. With the introduction of rosin alum sizing, the use of acid resistant fillers became common. China clay or kaolin was the most common mineral, although other materials such as talc were also used. These fillers were used to improve certain paper properties but mainly to reduce production costs.

It was not until the mid 20th century that work began in earnest to study the possible use of calcium carbonate as a filler. The availability and cost of this mineral made it a very attractive alternative to the European papermaker, although in the United States, kaolin remained the cheaper option. Research looked into alternative sizing systems, and in 1958, Hercules started manufacturing an alkylketene dimer (AKD) product under the trade name Aquapel, which was suitable for sizing paper under alkaline conditions.

As is typical with the paper industry, take-up of this new technology was slow, but in the 1970's and 80's, the European paper industry began to fully embrace neutral or alkaline papermaking, and the use of calcium carbonate as a filler grew dramatically. Although this move was driven by financial considerations, there were considerable side benefits. The permanence of the paper improved dramatically; sheet brightness increased; sheet strength improved; filler levels could be increased; and opacity was enhanced. Engineers also found that corrosion on the paper machine was dramatically reduced.

There were a number of different sizing chemistries tried during this period, but three systems were generally accepted across the industry by the end of the 1980's. These were variations on rosin to allow it to work up to pH 7.0 – the so called neutral rosin sizing; and two reactive sizes – AlkylKetene Dimer or AKD and Alkenyl Succinic Anhydride, or ASA.

The other major change at this time took place in North America. As I mentioned before, the price of kaolin was less than calcium carbonate in this region, as there are only limited natural deposits of this mineral in the region. This fact led to the development of precipitated calcium carbonate in the 1960's. In the mid-80's, Pfizer (now Specialty Minerals Inc. – SMI) built their first on-site PCC plant at a major US fine papers mill. This immediately gave both financial and quality benefits to the mill, but enforced an alkaline conversion. Satellite PCC plants are now common across the globe.

So – this is the background to our meeting today, some quarter of a century later. In just two days, we will try and delve into the impact these changes have had on wet-end chemistry, and to look at how the technology can benefit us in manufacturing paper here in India.

Acid to Alkaline Conversions

During my time working with alkaline systems, I have seen trouble free conversions, and I have seen those that experience a huge number of problems – with consequences of increased expenditure and losses on behalf of both the suppliers and the paper mills. The lesson that I have learnt from this, is that to ensure a trouble free conversion, there needs to be both good planning and a commitment from all involved – and that means investing in the conversion.

As a supplier, I have authorised \$250,000 in equipment alone for a conversion, and have calculated that in one case we spent about \$400,000 in supporting a conversion at a major mill. For a supplier to commit to this amount of money, there also needs to be a strong commitment from the mill management to that supplier, and to the conversion as a whole. The result of that commitment though is extensive planning, team building and a trouble free conversion.

On the other hand, I have also seen mills who ask more than one supplier to trial, who ignore the advice of their (hopefully experienced) suppliers, and refuse to make any investment on their own part. As a consequence, the suppliers cut back their commitment – as it was a risky venture – and the trials resulted in machine downtime and lost production. Neither the supplier nor the mill was satisfied with the results.

Is this applicable just to large mills? By no means! One example that I was involved with was on a 3-4 tonne per hour speciality paper machine. The mill committed to pay a premium for their chemicals from a single supplier, and chose to convert to an ASA sizing system – which involves much more equipment than an AKD system. The detailed planning took several months, and on the day of the conversion, the mill started up the machine under alkaline conditions, producing a higher quality paper, at a lower cost than before. Within 24 hours, it broke its first production record, and continued to break record after record over the coming year.

So – the lesson learnt – planning and commitment is essential for a trouble free conversion. Now let's look at the wet-end chemistry in more detail.

One major benefit of the global move to alkaline papermaking is that there is a lot more chemistry. This might seem like bad news to the paper mill and good news to the supplier – but in fact it is good news for us all. Under acid conditions, any chemicals had to work with high levels of aluminium sulphate present and high conductivity. This limited the performance and types of chemicals that could be used. With the move in pH, and the removal of all that alum, there appeared a lot more chemicals that could perform well. Virtually all research into new chemistry is now carried out at neutral and alkaline pH, and the developments are exciting.

Retention and Dewatering

I have used the term dewatering here rather than drainage. The reason for that is very simple – free drainage really only takes place during the early stages of the papermaking process. This is followed by vacuum dewatering and then pressing. Most papermakers are interested in the total dewatering and the moisture after the press section. This is affected by the wires, felts, table set-up, wet-end and press design, and of course, chemistry.

So let's look at how chemistry can affect this. First of all it is important to point out that there is an inter-relationship between retention, dewatering and formation – and changing one almost always has an impact on the other two.

Almost every additive in the wet-end can affect retention and dewatering – including fibre, filler and water – but before looking in more detail at the chemistry, let's focus for a moment on these materials – and the physical size of them.

A number of authorsⁱⁱⁱ have taken the basic paper system and magnified it 10,000-fold. On this scale, the size of a single hole of the wire screen is about 2.5 m x 2.5 m. A softwood fibre would then become similar to a full sized tree trunk – 30 metres long and 50 centimetres thick. The fines would be similar to twigs, leaves and even pine needles, and the filler would be like fine gravel.

We now add the chemicals, and find that a polyacrylamide retention aid is just 15 cm long, but still microscopically thin; polyethyleneimine is 6mm in diameter and 0.15mm thick; pigment particles are less than 5 cm in diameter; and size emulsion droplets are less than 2 cm in diameter.

It is difficult to comprehend how such small components could be retained on this magnified scale, much less act as they do! Such a picture motivates us to understand the importance of colloidal and surface chemical forces in retention chemistry. Such an understanding will also make us realise that every part of the process has an influence on all the other parts. This means that changing the addition point, or the dosage of one chemical, can have an impact on many other parts of the operation. To operate in such an environment requires teamwork, and good management of the wet-end.

Aluminium salts

Aluminium sulphate, or "papermaker's alum," has for almost two hundred years been a general remedy for almost all problems encountered in the papermaking process. Alum has been used as a sizing agent in combination with rosin, as a mordant for dyes, as a retention aid, to fight pitch troubles, and as an agent to control pH.

In spite of the fact that many new chemicals have been introduced into the alkaline papermaking process at stages where alum was previously applied, it still remains important in a number of applications. That is why each papermaker should still know basic aluminium chemistry.

In addition to alum, another aluminium compound is seeing increasing use in papermaking. Polyaluminium chloride or PAC is commonly seen in alkaline systems as it permits aluminium-assisted processes to be run at these higher pHs, a feature not possible with conventional alum.

So is there any point in using alum in an alkaline environment? Well yes there is – especially for retention and dewatering, but also for sizing. To explain this a bit more, let's look at the other retention chemicals in common use.

Retention and Dewatering Aids

For many years polyacrylamides have been used as retention aids. These polymers can be manufactured with different molecular weights, structures and ionic charges. This makes them a very versatile chemical. As a retention aid, they are typically added after the screen on the paper machine, giving no more than a second to form flocs and capture fine particles. The nature of the charge on the polymer does vary depending upon the wet-end chemistry. In fine paper applications, the biggest factor in this is the filler. PCC and many other fillers that contain no dispersant are often marginally cationic. This means that an anionic polymer works best. If there is a polyacrylate dispersant present however, then the filler appears to be strongly anionic, opening up the opportunities for a cationic polymer to perform better. If waste paper or wood fibres (eg TMP, CTMP, etc) are included, then again a cationic polymer usually works best.

Using single component systems can enhance both retention and dewatering - which in turn have an effect on formation. Greater control over these different factors can be obtained with a dual system however. These usually involve an initial high charged, low molecular weight cationic polymer such as a polyamine, polyDADMAC or polyethyleneimine, followed by a high

molecular weight polyacrylamide. These can work well, but another approach has gained acceptance over the last decade – microparticle systems.

Microparticle systems

The first two mainstream systems were Eka's Composil system, and Ciba's Hydrocol system. Composil comprises a high molecular cationic polymer (usually starch or polyacrylamide) followed by anionic silica, while Hydrocol uses bentonite instead of the silica. A number of other systems have come onto the market now, but these two approaches still dominate globally.

There are a number of explanations as to how these systems work. A scenario that I like is that the high molecular weight polymer is added before the fan pump, forming large flocs. These are torn apart by the shear forces of the pump and screening process, before being rebuilt through the addition of an anionic micro-particle. This floc is not particularly strong, but is sufficient to pass through the headbox slice and onto the wire.

Here, the water around the floc drains rapidly, but the water within the large floc is held in place. As the water leaves the sheet, the floc's stability starts to degrade, and the floc falls apart, releasing the water held within. By this time, the sheet is at the vacuum boxes, which can now exert a greater degree of suction on the smaller flocs remaining, thus removing more water. Once in the press section, the pressure can extract even more water.

What this does, is allow better free drainage, and then better vacuum and press dewatering, thus giving a lower water content leaving the press-section. The sheet in turn has better formation and higher retention numbers are seen. This is an ideal situation, so long as it is set up and optimised properly – but it is more expensive than a single or dual component system, and is not suitable for every machine system.

One other, low cost approach, is to use alum. This does not always work, but I have seen extraordinary results in some mills. Alum, as we know, is an acidic, cationic solution. If the pH of the solution is raised, the alum starts to come out of solution as aluminium hydroxide, and also starts to lose its cationic charge. This may seem a problem in an alkaline system, but we can use it to our advantage. If we in-line dilute the alum with clean fresh water, so that the pH comes above say 5, then we see a precipitate of aluminium hydroxide. If there is enough water, and this is done very fast, then the particles are of a nano-particle size. They will also maintain a cationic charge for a period of up to two minutes. This means that if we add this to the thin stock on a paper machine, we are in effect creating and adding a cationic microparticle material. This very cheap and effective adaptation of the standard approach may need to be optimised – but it can produce dramatic results, especially if an anionic retention aid is being used. Indeed some microparticle suppliers suggest using alum or PAC with their systems to further enhance performance.

Sizing

There are two types of sizing seen on paper and board machines – internal and surface sizing, and they each have their role in papermaking.

Sizing is an important part of the wet end chemical operation, but the papermaker needs to have a clear understanding as to why he is sizing the paper. Indeed, this is a question I often ask paper mills I visit, and sometimes the answers can be very different from person to person, and often quite surprising.

In all applications I have come across, the purpose is to modify the surface of the fibres to control the penetration of aqueous liquids into the paper. The penetration usually correlates with the absorbency, repellency (hydrophobicity), and spreading of the aqueous liquid concerned. Control of these important properties can be required for three purposes:

1. Control of the penetration rate of the aqueous phase in a converting operation such as size press treatment or coating. Indeed in the period between the fountain pen and the advent of the ink-jet printer, many North American papermakers manufacturing xerographic papers added just enough size to ensure runnability at the size press. There was no other requirement for sizing beyond that.
2. Control of liquid absorption or wetting in a printing process; and
3. Control of the performance of many grades of paper and board, e.g., milk carton, packaging papers, wallpaper, etc.

It is essential to the paper manufacturer that end-use requirements are met, and that the degree of sizing of the product remains as constant as possible until ultimate consumer use or converting. This can mean considerable work to balance the levels of internal and surface size. Indeed I could give a full paper on this subject alone, but I am afraid that time does not permit that today.

Although in most cases the purpose of internal sizing is to prevent quick penetration by water, occasionally it is needed for the control of penetration of other fluid types, e.g. acids, alkalis, oils, alcohols, chemical dispersions, etc. It should be noted that good resistance to one fluid does not necessarily mean resistance to another. The applicability must be ascertained by specific tests using the fluids concerned.

Before looking at the main neutral and alkaline sizes, what are the requirements for a good internal size? I believe there are six factors:

1. The size must be readily available and chemically stable
2. It must be possible to add in a form that ensures good and even distribution across the papermaking fibres.
3. The size must be retained in the wet end, and must attach itself in some way to the papermaking components in the sheet.
4. The molecules must orientate themselves so that the hydrophobic end is away from the fibre.
5. The size must be sufficiently hydrophobic so that sizing is achieved in a cost effective manner.
6. The size must not cause unacceptable problems in the paper or board manufacture, nor in the subsequent conversion or use of the paper.

Rosin

Rosin size as we know has been in use since the mid 1800's. Most rosin is extracted from tall oil, a by-product of the kraft cooking process. By distillation it is possible to obtain a fraction that contains a high level of abietic acid. This in turn is partially reacted with either maleic or fumaric anhydride to produce a fortified rosin.

The rosin can be reacted with metal ions such as sodium or potassium^{iv} to form a liquid soap, and then precipitated in the wet-end with aluminium ions. This approach requires a low pH, and even then sizing can be inefficient – especially in hard water areas where calcium and magnesium ions interfere with the sizing.

Another approach is to make an emulsion or dispersion of the rosin. The use of these products has grown dramatically in recent years, as they offer the ability to size at pH values up to, and in some cases exceeding 7.0. Rosin emulsions do not actually react with aluminium ions in the wet-end, so there is no natural retention. For this reason, the emulsions are usually stabilised with a cationic polymer which enhances retention, but also provides a lower melting point for the rosin.

The use of a mordant is still necessary though, and this can be either alum or polyaluminium chloride (PAC). The aluminium rosinate complex is not formed at the wet-end, but occurs in the driers^v. The rosin emulsion first breaks, and then the rosin melts and flows across the fibres. Finally, the rosin reacts with the aluminium species. This gives more efficient and more uniform sizing than is obtained with the soap version.

Although alum is used in acidic systems, the use of polyaluminium chloride allows the rosin to be used at higher pHs. PAC remains highly cationic at neutral pH and can aid rosin retention as a result. It also has an advantage in not adding sulphates to the system. As the pH rises, the tendency for the PAC to convert to aluminium hydroxide increases however, at which point the mordant properties cease. For this reason, most dispersed rosin applications are run between pH 6 and 7, but in some applications, pH's as high as 7.5 are achieved.

AKD

As I mentioned before, Alkyl Ketene dimer (AKD) has been used in the paper industry as a sizing agent since it was developed in the 1950's. ASA first appeared in the early 1960's, but did not becoming common until the mid 80's. Both AKD and ASA are commonly described as reactive or alkaline sizes because they form covalent bonds with cellulose, and neutral or alkaline pH values are employed in the papermaking system.

AKD is usually manufactured by chlorinating a fatty acid using phosphorus trichloride followed by the dimerization of the resulting product^{vi} with triethylamine to form a waxy solid material. This is melted and then emulsified with cationic stabilisers such as cationic starch or polymers. Since AKD has a relatively slow rate of hydrolysis when compared to ASA, this operation is

carried out at a central manufacturing facility, and the emulsion or dispersion is then shipped as a ready to use product to the paper or board mill.

There has been considerable research into both the mechanism of AKD sizing and its performance on the paper machine. To go through even a part of that would take days, but some of this work has produced very interesting results.

- The choice of emulsifying agent can affect the shelf life of the AKD, as well as the on-machine performance^{vii}
- Only a very small amount of added AKD (probably less than 20%) actually reacts with the cellulose and contributes to sizing^{viii,ix,x}
- Since AKD is a wax, excessive amounts of this size can cause slipperiness on the sheet. This can be overcome if there are unsaturated groups within the hydrocarbon tail of the size. Alkenylketene dimer products have been used effectively instead of AKD for this purpose.^{xi}
- The relatively slow reactivity of the AKD can mean that the sheet is unsized by the time it reaches the size press. This has led many papermakers to over dry the sheet to achieve some curing. Full cure in the paper or board may not occur until some hours after the sheet has been manufactured. The curing of the AKD can be enhanced through the addition of a cationic polyamideamine-epichlorohydrin resin or bicarbonate ions to the wet end^{xii}.
- The unreacted AKD in the sheet at the size press may offer benefits to sizing. The AKD may migrate^{xiii}, possibly through vapour phase transmission, into the starch and react with the hydroxyl groups there. This can result in greater sizing than could be obtained if the sheet was fully cured before the size press.
- The presence of free ketones in AKD sized paper can contribute to deposits in subsequent processes that involve temperatures sufficiently high to volatilise the ketones, such as xerography.

Finally a mention of fugitive sizing. In the late 1980's and early 1990's, it was found that paper containing PCC filler, could lose its sizing with time. Considerable research went into the mechanism and various promoters were found that reduced, but did not eliminate the problem. The cause was eventually traced to free lime present in the PCC, and now PCC manufacturing processes have been improved to ensure that this is no longer an issue.

ASA

Alkenyl Succinic Anhydride is produced from the reaction of an isomerised olefin with maleic anhydride^{xiv}. The maleic anhydride molecule supplies the reactive anhydride functionality to the ASA, while the long chain alkyl portion provides the hydrophobic properties associated with this size. The resulting succinic anhydride group is extremely reactive, and will complex with hydroxyl groups on cellulose, starch and water. It is the ASA molecule's high reactivity that provides some of its major advantages.

The reactivity of the ASA means that the product will readily cure on the paper machine without excessive drying or the use of promoters. This means that

most of the cure is achieved before the size press, so allowing the papermaker to dry the sheet normally, rather than over drying as described above. This can give greater control of starch pick-up at the size press, full sizing at the reel and improved productivity. It may however mean that sizing (certainly as measured using a surface method such as Cobb) will not be as great as could be obtained with a size that does not cure fully before the size press – such as AKD (see above).

Another issue caused by this reactivity is the tendency of the ASA molecule to react with water. This forms a di-acid, which is hydrophilic at one end of the molecule and hydrophobic at the other end. The di-acid has the ability to react with metal ions such as calcium or magnesium that are often found in water systems. The products of these reactions are sticky precipitates, which could potentially deposit on the fabrics and frame of the paper machine, although it has been shown^{xv} that the calcium salt can contribute to sizing. The aluminium salt is much less tacky however, and the presence of an aluminium source in the system is consequentially of great benefit. This ability to react with metal ions has been exploited in some mills, notably in Japan, where a potassium salt of a low molecular weight ASA is made and then precipitated onto the fibre by using alum at acid pH in much the same way as rosin is used.

Much of the development work with ASA sizes in the 1980's was targeted at ensuring that ASA was easy to use in practice in the mills. In depth studies^{xvi} ^{xvii} ^{xviii} of the reactions that take place in the stock and white water systems of mills, have led to the development of programmes that are simple to use and which ensure that ASA hydrolysis is kept to an absolute minimum. This ensures high sizing efficiency, low costs and good machine runnability.

Application

ASA is supplied to paper and board mills as fluid oil, which on its own has no charge and no great affinity for the anionic cellulose fibres. To ensure good retention, it is emulsified in a cationic carrier and then added to the thin stock system of the machine.

As is shown by its use in many processed foods, starch is an excellent emulsion stabiliser, but the correct choice of starch is critical. Cationic starch is often used in paper mills, to give improved dry strength, higher retention and sometimes even drainage. This means that if we use this as our emulsifying agent for the ASA, we should see the following benefits:

- Ease of emulsion preparation
- Stable emulsion
- Affinity for the paper making fibres
- Size retention
- Size promotion
- Improved dry strength

The other benefit of cationic starch is that it is available in a variety of forms, molecular weights and with a choice of cationicities. For these reasons, many mills view the starch as a key component of the sizing system.

There are several choices on the form of cationic starch available. The choice of this will often depend upon the mill, its location and size, and economic factors.

- Liquid starch
- Cold water soluble powder starch
- Cooking powder starch

Liquid Starch

These starches are low molecular weight starch solutions, produced at about 20-25% solids. These are excellent products for mills that do not have the facilities to make up either of the other two starches. The great advantage of this starch is that it is delivered as a liquid, and needs no further treatment. It can be fed directly to the emulsifier.

There are a number disadvantages to the liquid starch however:

- It has a low molecular weight and so does not give as stable an emulsion as a cooked starch, especially in hard water areas
- It has a high cost, which means that it cannot be used at the levels required to act as a promoter. This is generally not such an issue in recycled board but is more important in fine paper applications
- It is often very viscous, creating handling issues
- Shelf life is short (generally no more than 90 days, and often much less in hot climates)
- Only a limited number of manufacturers produce this grade of starch

Cold water soluble starch

Cold water soluble or pre-gelatinised starch, is a powder that has been treated to dissolve in cold water. This makes it suitable for those mills that do not have a starch cooker, yet which are too far from the liquid starch manufacturer to justify the shipment costs.

These starches are normally dissolved, either using a manual or a fully automated system, in cold (ambient) water, at 3-5% dry solids. Increasing the water temperature (to ~30°C) does increase the rate of dissolution, and helps prevent lumps of undissolved powder.

Cooked starch

Cooked starch is by far the most commonly used emulsifying agent for ASA, and generally outperforms the other two options. These materials are supplied as a powder, and dispersed in cold water. The cooking can be carried out either in a batch process or semi-continuously in a jet-cooker

The starch is cooked typically at 4-12% solids and “quenched” with further water to bring the solids down to 1-5%. For ASA emulsification, it is normally

recommended that 3-5% starch is fed to the emulsifier, but this depends upon the starch properties.

Polymer

Polymers also have a place in this technology. They too can be produced in a range of molecular weights, with a choice of cationicities and in different forms. They are also common in paper mills, as retention and drainage aids, and for other applications.

Most size suppliers also make synthetic polymers, but relatively few are basic in starch products. The reasons for this are based on economics, and the other potential markets for starch. This means that there has been considerable work undertaken to study synthetic polymers and to establish this technology in the industry.

The most common chemistry of these products is based on cationic polyacrylamides, although polyamine, polyamide and polyDADMAC chemistry have all been tried. Considerable success has been achieved with some of these products, but never (so far) to the level achieved with starch. They do however have some considerable benefits.

- Easy to handle liquid polymers
- Limited contribution to COD and BOD levels
- Can be produced with a broad variety of properties
- Available globally

There are a number of issues that have been seen with these polymers:

- Usually low solids, so high shipment costs
- Low emulsion stability – especially under shear
- Reduced promotion of the ASA sizing mechanism
- More expensive than using cooked starch
- Polymer content of the emulsion is much lower than the starch content would be.

Despite this, a number of mills are running polymer programmes very successfully, especially those mills that do not have a cooker for cationic starch. In those cases, the capital costs involved in installing such a cooker make the polymer option a more attractive economic proposition. Those mills that do use polymers for emulsification, need to set up their equipment in a different way to ensure optimum results.

Equipment

Emulsification systems generally deliver a controlled and predictable ASA emulsion. They are designed to ensure safe, trouble-free, and maintenance-friendly operation, and to integrate with the mill's process control systems. Although generally only starch and ASA are fed into the unit during normal operation, many manufacturers include a water and caustic inlet for cleaning purposes.

The emulsifier comprises an ASA size pump and meter, starch flow measurement and control, and an emulsifying turbine. The turbines are usually pumps which were designed to transfer water at high pressure, but it was discovered that they can also produce a high quality emulsion. Included on the units are flow meters, pressure regulators, and control valves for starch, water, and (when required) caustic. The electrical panel enclosure contains the motor starters, control logic, and instrumentation for operation in either a manual local control mode or automatic mill interface control mode. The emulsion produced is discharged either directly to the paper machine, to a manifold system feeding several machines or plies, or less commonly, to a holding tank.

Approach

The key to good sizing with these systems is to ensure that the ASA does not hydrolyse before it is retained in the paper sheet. This means that the mill must pay attention to a number of key areas:

- Keeping the ASA dry before it is used
- Emulsifying and using the emulsion immediately afterwards
- Using cool starch (40°C max) to emulsify with
- Acidifying the starch so the emulsion pH is low
- Adding the emulsion to the correct addition point on the paper machine
- Maximising retentions on the machine
- Managing the wet-end chemistry

If all these areas are managed correctly, a very efficient, low cost sizing system results, as can be testified by the many mills globally that are running systems like this.

Other additives

Biological activity in the water system may dramatically increase as pH, temperature and the quantity of nutrients increases. This is often combined with a growing level of filler and similar materials that can act as a seed on which bacteria can grow. This may lead to a higher usage of biocides, certain types of which have been shown to impact sizing.^{xix} The other key difference seen by mills converting from acid to alkaline is the type of biocide needed (as well as the quantity). This is because fungi are more common in acid systems, whereas other life-forms predominate in alkaline systems, which require different approaches to treatment. As a result, many mills have found that their biocide costs can double or treble following a conversion.

Defoamers are another interesting area of discussion. Reactive sizes tend to be more sensitive to additives than rosin (although it may be the alum counteracting the effects of these other materials). This means that the choice of defoamers must be carefully made. Typically silicone defoamers do not harm sizing chemicals at the addition levels normally seen. Oil based defoamers do tend to be harmful to sizing however.

The higher cationicity of AKD compared to ASA tends to mean that higher dosages of defoamers are needed, but in any event this is usually less than

under acid conditions. I do know mills which have converted to ASA where the defoamers have been switched off entirely, or reduced by over 90%.

Other factors

A number of studies^{xx} have looked at the effect of fines from different furnishes on sizing. These have found that it is the surface area of the fines that impact sizing rather than the mass of fines. In a secondary fibre furnish, the level of fines is known to be considerably higher than in a virgin pulp system. The extra physical treatment that the fibres and fines will have experienced will increase the surface area and in turn increase the sizing demand in that paper or board. The type of fibre, previous treatments of this fibre and the number of times it has been previously recycled will impact the extent of this effect.

Another study^{xxi} found that sizing is more effective when attached to the fibre rather than the fines, so one of our objectives in optimising sizing in any system should be to maximise the quantity of size on the fibres. Since the higher surface area of the fines makes their apparent anionic charge greater than that of the fibre, the tendency for any cationic additive to attach to these particles is obvious. This means that we have to seek an approach that reduces this attraction, to optimise size performance. The use of highly cationic polymers as scavengers or charge control agents has been very effective in addressing this issue.

The table below^{xxii} shows some examples of how ASA sizing is affected by different grades of secondary fibre. The secondary fibre in these cases is generally mixed office waste that has been de-inked, although in one case old newspapers and magazines were used.

This indicates that in these cases the recycled fibre itself is unlikely to be the major factor in those mills that experienced increased size usage, but rather the materials that accompany the fibre, such as de-sizing extractives. Materials of a similar nature have also been found in virgin pulp^{xxiii}, especially those that are bleached with hydrogen peroxide. Data from a number of mills has been examined to look at this in more detail.

As the conductivity of a water system increases, it is well known that the performance of functional chemicals (e.g. size, strength resins, etc) in the system deteriorates. In many cases, this is due to the impact of inorganic ions on the cationic charge of the chemical in question. Higher chemical usage, along with the high level of fines can lead to foaming issues and a consequential increase in defoamer or antifoam usage.

Grade	Recycle Content (%)	Impact on ASA sizing	Comments
Office grades	Up to 25% from on-site de-inking plant	No impact on sizing or size usage.	Main issues related to stickies in felts. Resolved by changing source of waste.
Office grades	Up to 20% post consumer waste or 10% purchased de-inked pulp.	Up to 20% increase in ASA size usage to obtain same results	
Scholastic grades	100% from on-site de-inking of old news and magazines.	100% increase in ASA size usage.	Main cause of increase in sizing due to very high levels of de-sizing extractives in de-inked pulp.
Offset grades	25% purchased de-inked pulp.	No impact on sizing	Main size test is the Bristow Wheel.
Offset and cover stock	20-80% purchased de-inked pulp.	Sizing is significantly improved through using recycled fibre.	Virgin peroxide bleached sulphite pulp that is normally used, is difficult to size.

Closing remarks

So is it all worthwhile? Well the answer that many mill executives would give is a resounding Yes! I have seen enormous savings in costs by making this change, and not just in large mills.

I would like to finish by just mentioning one small mill, producing about 70 tonnes per day of speciality papers. This mill converted from rosin alum to ASA about ten years ago. At the time, the commercial pressures were significant, and the mill management had to either change or close the mill. They decided to change – and converted to alkaline papermaking.

Planning was intense, but using experienced suppliers, they were able to draw on many years of knowledge. Mill personnel were all trained – from stock preparation through to sales and marketing; new equipment was ordered and installed; and new raw materials sourced – all in ten weeks.

The mill started up on a coloured grade, yet exceeded all specifications within fifteen minutes of putting stock on the wire. Quality was better in all aspects, including formation, sizing, strength and sheet appearance. Machine runnability and cleanliness were better than under acid conditions, and the retention polymers ensured better dewatering, and so faster machine speeds. Productivity started increasing immediately. Ash content was doubled within a few months. The cost per tonne of paper fell as a result of all these factors.

The improved sheet quality became apparent very quickly in the market, and the order book began to fill. Within a year, it was possible to raise prices as a means of controlling demand. Finally, the mill began to develop new grades of paper that they were not able to make before. Generally these were high value products, and so again, profits were increased.

Now ten years later, the mill is still thriving. The market is no longer as kind to it as it once was, and most of the management have been promoted to other mills in the group, but the operation still remains profitable and continues to produce high quality papers for niche markets. This is just one example of many where the mill executives would resoundingly say that converting was relatively painless and certainly worthwhile.

So may I finish by thanking you once again for inviting me to speak, by encouraging you all to keep optimising your paper and board machines through the use of innovative chemistry, and by requesting the chemists here to keep developing the next generation of chemicals that will enhance papermaking in the years ahead. Thank you.

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