A REVIEW OF ADVANCES IN INTERNAL SIZING OF PAPER

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INTRODUCTION

The term sizing, as used by papermakers, is somewhat ambiguous. It is used to refer both to the control of water penetration in the body of a sheet of paper or board (internal sizing) and also to the control of penetration through the surface of the sheet (surface sizing). The latter is strictly a surface modification and is therefore performed as a dry-end process. Internal sizing on the other hand, because it is intended to modify the water absorbing properties of the component fibres in the body of the sheet, is necessarily a wet-end operation. This review is concerned only with internal sizing.

Internal sizing, when successfully performed, retards the rate of penetration of a fluid through capillaries formed both within and between fibres. The fluid of importance is, for most commercial grades of paper, water but resistance to non-aqueous fluids is also important in some applications. However, the present review will concern itself only with sizing against aqueous systems.

The penetration of water into paper is influenced by a number of factors, not least of which is the sheet structure and porosity. In some cases this can be a more dominant effect than the hydrophobicity of the component fibre surfaces. Sheet structure can be controlled to a large extent by the selection and refining of the pulp, and a discussion of its importance can be found elsewhere (1). Structural considerations notwithstanding, the absorption of fluids by paper can be considered to be a combination of both surface wetting and of capillary pore penetration.

Wetting and penetration of porous solids

If, when a liquid drop is placed on a smooth surface, the forces of adhesion between the solid and the liquid are greater than the forces of cohesion of the liquid, then the liquid will spread spontaneously and will perfectly wet the surface. If the forces reach an intermediate balance, the liquid drop will form a definite contact angle (θ) with the solid surface (figure 1).



Figure 1

This wetting process can be described in terms of a balance of specific surface energies - the Young equation (equation 1).

$$Cos \theta = \frac{(\gamma_{sv} - \gamma_{sl})}{\gamma_{lv}}$$
 Equation 1

Where γ_{sv} , γ_{sl} , γ_{iv} are the solid-vapour, solid-liquid and liquid-vapour interfacial tensions respectively.

When a liquid contacts a porous solid, the liquid in contact with the pore becomes curved due to differential tensions. For a pore of cylindrical cross section, the pressure difference, ΔP , across the curved surface can be expressed in terms of the contact angle, the liquid-vapour interfacial tension, and the radius of pore (equation 2)

$$\Delta P = \frac{2\gamma_h \cos\theta}{r_c}$$
 Equation 2

Where r_c is the radius of the cylindrical pore. Clearly, if the contact angle between the solid and the liquid is greater than 90°, ΔP is zero and the liquid will not penetrate by capillary action. However, this equation defines an equilibrium position, and sizing is more concerned with the dynamic process of penetration. The dynamic rate of capillary rise of fluids into paper has been effectively described by models of penetration of fluids into a single capillary - the Washburn equation (equation 3). This gives a good approximation to the rate of capillary rise of non-swelling fluids into paper (2). Modifications of the basic equation are necessary to describe the behaviour of swelling fluids such as water (3).

$$l^2 = \frac{\gamma_{lv} r_c t Cos\theta}{2\eta}$$
 Equation 3

Where 1 is the distance penetrated into a cylindrical capillary of radius r_c in time t by a liquid of surface tension γ_{iv} and viscosity η .

These approaches assume that the penetration of a fluid into paper is analogous to that of a fluid into a single capillary. Retardation is thus brought about by the creation of a low energy, hydrophobic surface at the fibre-water interface which increases the contact angle formed between a drop of liquid and the surface and thus decreases the wettability. Contact angles have been shown to be sensitive to molecular packing, surface morphology and chemical constitution (4-6), and it is the latter which is influenced during the internal sizing of paper. An excellent review is available elsewhere (7).

The introduction of hydrophobic groups onto the fibre surface is the essential step in all internal sizing and it has to be done in a way which will allow a good distribution of the sizing molecule through the body of the sheet but which will not interfere with interfibre bonding (cf. fibre softening agents). Thus internal sizes are introduced at the wet end of the papermaking system, usually as colloidal suspensions, which are retained in the fibre network during sheet formation. During drying, and to some extent afterwards, they are able to migrate and undergo some form of interaction with the surface which allows orientation of the hydrophobic group and the creation of a low-energy surface. Unless the molecule is anchored to the surface by strong (ideally covalent) attachment, molecular overturning is possible. Such effects have been demonstrated for sizing by fatty acids and the rate of overturning of saturated fatty acids has been shown to increase as the alkyl group chain length decreases ($\underline{7}$).

Internal sizing

The internal sizing process can be considered to take place in three distinct phases. Firstly, the retention of the amphipathic sizing molecules by the fibres during the wet formation process. Secondly the spreading of the size molecules over the fibre surfaces. and thirdly their orientation at the fibre surface so as to create a low energy hydrophobic surface. Retention at the wet end is achieved by electrostatic interaction between a particle of size emulsion and the fibre surface. It is important that at this stage the size molecules do not spread over the surface and become oriented as happens in the case of water soluble guaternary ammonium salts with hydrophobic alkyl groups which are used as softening agents. This would have the effect of interfering with interfibre hydrogen bonding between the surfaces of the fibres which takes place during consolidation and drying of the wet web and which is necessary for the creation of strength. In the second stage of the process, i.e. the spreading of the retained size over fibre surfaces, the physical properties of the size molecule are probably of crucial importance. The molecule must be sufficiently stable to resist hydrolysis and yet mobile enough, under the conditions of drying to cover fibre surfaces. Finally, for orientation to be achieved, some form of strong interaction between the polar end of the sizing molecule and the fibre surface. either electrostatic or covalent, is required.

Sizing systems and pH

Prior to the beginning of the 19th century the penetration of aqueous solutions into paper was controlled solely by surface treatment with water soluble polymers such as gelatin. The addition of hydrophobic chemicals into the wet fibre suspension (internal sizing) was a major departure from established methods and was first introduced in the early nineteenth century using saponified rosin in conjunction with aluminium sulfate. Aluminium sulfate gives rise to an acidic solution with a pH of typically around 4-5. Paper was sized by this acidic process for over 150 years until the early 1970's when the next important change in internal sizing technology took place. This arose because of the need to size paper at neutral to slightly alkaline pH.

The driving forces which caused papermakers to change from acid to neutral paper making at this time have not always been easy to identify, but probably the most important factor is that neutral pH allows the use of calcium carbonate, a relatively inexpensive and good quality filler. The availability of good quality non-abrasive carbonate in Europe is probably the reason why neutral paper-making has developed more rapidly there than in North America where the natural grades of calcium carbonate are rather abrasive for papermaking applications and can cause excessive machine wire wear. However, the situation in North America is changing quickly as a result of the increasing use and commercial competitiveness of precipitated calcium carbonate (PCC). PCC is produced by calcining natural limestone to calcium oxide which is then converted to calcium hydroxide by the addition of water. Carbon dioxide, from the flue gas of the steam raising plant is then used to precipitate the calcium carbonate. The carbonate can, by correct control of the precipitation process, be obtained in various crystalline forms, particle sizes and surface areas which give it significant advantages over ground calcium carbonate. Although inherently a more expensive product than ground calcium carbonate. PCC's can be cost effective because they are produced on-site in satellite plants which do not require the slurry to be dried, and because they offer improved performance. Because of the buffering effect of calcium carbonate, they cannot be used in conventional acidic rosin alum sizing and modifications are needed to allow its use in that system, these are discussed later in this review.

The trend for increased use of recycled fibre also makes it more difficult to size paper at low pH because of the higher levels of carbonate being introduced into the system. The effect of this in Europe (where levels of recycling are very high) has been to change papermaking from almost totally acidic to almost totally neutral within a 20 year period. The same change is also happening, in the USA, Canada and Scandinavia, although less rapidly because levels of recycling are lower. However, recycling technology is now firmly established and it is difficult to foresee a return to acidic paper making. There are other advantages of neutral papermaking, but these have probably not been so commercially influential in the change. Savings, particularly in energy costs and in water purification have been demonstrated (8) and permanence has been shown, by accelerated ageing experiments, to improve (9-11). Rosin sized paper is, however, more susceptible to UV degradation (12). Other important advantages of neutral papermaking which are often quoted, are reduced machinery corrosion, and increased paper strength which arises from the increased swelling that occurs at high pH. The latter also allows less energy intensive refining. However most of these changes should more correctly be considered to be advantages which arise from operating at higher pH rather than from the change of sizing system.

Sizes have therefore been developed which are capable of functioning in a neutral papermaking environment. One approach has been to modify the acidic rosin sizing process to enable it to be used at neutral pH, but there has also been an entirely new approach to the problem of introducing hydrophobic groups to fibre surfaces which involves the use of new sizing molecules. These depend upon covalent attachment to the hydroxyl groups of the fibre surface through reactions such as esterification, a general reaction scheme for which is shown in figure 2.



Some of the more common compounds which have been considered for sizing by direct covalent reaction, but not always used commercially, are shown in Table 1.



Table 1.

 ⁽a) German Patent 2,423,651 (1974); (b) German Patent 2,611,827 (1976); (c) German Patent 2,611,746 (1976); (d) US Patent : 4,123,319 (1978); (e) British Patent 954,526 (1964) (f) Canadian Patent : 770,079 (1967); (g) US Patent 3,102,064 (1963); (h) US Patent 3,409,500 (1968); (i) US Patent 3,455,330 (1969); (j) US Patent 4,207,142 (1980) (k) US. Patent 2,627,477, (1953); (l) US Patent 2,785,067 (1957); (m) US Patent 2,762,270 (1955); (n) US Patent 2,865,1743 (1958); (p) US Patent 2,961,366 (1960); (g) US Patent 2,986,488 (1961); (r) US Patent 3,483,077 (1969); (i) US Patent 3,050,437 (1962); (i) US Patent 3,589,978 (1962); (ii) US Patent 3,492,081 (1970); (v) US Patent 3,310,460 (1967); (w) US Patent 3,627,631 (1971); (x) US Patent 3,499,824 (1970); (y) US Patent 3,575,796 (1971); (u) US Patent 3,821,069 (1974)

The assumption, in these sizing systems, is that covalent linkage allows the permanent attachment of hydrophobic groups in a highly oriented state which makes sizing possible at very low levels. The main requirement of the molecule is that it has good stability towards water, since it is necessary to prepare it as a stabilised aqueous emulsion for use at the wet end, and that it also has good reactivity towards cellulose. These are, to some extent, mutually exclusive, and a compromise is therefore sought. A further discussion of this point is taken up later in this review. In addition, the selected molecule must have physical properties which allow diffusion and migration during drying and must be sufficiently chemically reactive at these temperatures to undergo reaction with cellulosic hydroxyl groups.

The most commercially successful of these sizes have been the alkyl ketene dimers (AKD) and the alkenyl succinic anhydrides (ASA). These are at opposite ends of the spectrum of reactivity and hydrolytic stability. AKD's are rather unreactive towards cellulose, except at elevated temperatures, but have good hydrolytic stability. The reverse is true for ASA's. The use of rosin at neutral to alkaline pH followed after the development of AKD and ASA for neutral pH sizing. The historical development of neutral papermaking and the development of the three main neutral sizing systems (AKD ASA and neutral rosin) has been the subject of several useful reviews (<u>15-20</u>).

ROSIN SIZING

Rosin is the natural resin of pine trees and has been used as commodity, for waterproofing of rope and boats etc., since the 4th century BC. Its primary source is as a sticky exudate from pine trees (gum rosin), but it can also be obtained as a by-product of the Kraft pulping process (Tall oil rosin). About 1.2 million tonnes of rosin are produced annually throughout the world, of which about 70% is gum rosin. The chemistry of rosin is extensive and complex and the reader is referred elsewhere for its general chemistry (21). Once volatile components (around 10%) have been removed from the natural gum, the glassy residue which remains is composed of a mixture of isomeric and structurally closely related tricyclic diterpene monocarboxylic acids (figure 3)



Figure 3

Abietic, palustric and neoabietic acids in total comprise about 46% of rosin. They are capable of isomerising to levopimaric acid which contains a conjugated diene structure that is able to react with compounds which have one or more carbonyl groups attached to carbon atoms that also make up a double bond. The Diels-Alder reaction of the diene with maleic anhydride is used to introduce additional carboxyl groups into the rosin in a process known as fortification (22). This is usually performed at around 0.25 moles of maleic anhydride per mole of rosin and therefore produces a mixture of reacted and unreacted rosin acids known as fortified rosin (23). The advantage of the process is that fortified rosins have a

lower softening point and are thus easier to emulsify. They also show improved sizing performance which may be due to the improved emulsion quality, to better retention or to more effective spreading over fibre surfaces during drying. Rosin is also sometimes treated with formaldeheyde to improve its resistance to crystallisation (24).

For use in the wet end of the papermaking process, the rosin is prepared in one of two ways. It can be saponified to produce the water soluble sodium salt (soap size) or it can be dispersed as the free acid in a suitable stabilising polymer to form an emulsion (dispersed size). The polymer may be anionic or cationic but, until relatively recently, casein - the anionic protein polymer from milk, has been used almost exclusively. The methodology of saponification and emulsification is well established and is adequately reviewed elsewhere (24). More recently cationically stabilised emulsions have been developed for use in neutral pH systems, and these are discussed later in this review.

Both the soluble carboxylate anion from saponified rosin and the anionically casein stabilised emulsion particles of dispersed sizes are anionic and therefore have a poor affinity for the anionic cellulose fibres. It is therefore necessary to use a mordant to fix the rosin species to the fibre surface. For many years this was done with aluminium sulfate, which gives rise to an acidic solution. The process became known as acidic rosin sizing, and is now discussed.

Acidic Rosin sizing

Acidic rosin sizing, although decreasing in importance, is a well established process and has been the subject of much research and review (24,25). Only a limited account will therefore be given here. Aluminium sulfate is used in conjunction with either a dispersed rosin emulsion or a saponified rosin acid solution. The hydrophobic rosin acid molecule is retained by the fibres by a primarily electrostatic mechanism (26) in which the alum plays a key role. The orientation of the size molecule at the fibre surface then takes place through the intermediacy of aluminium sulfate. No covalent bonding between the size and the fibre surface is believed to be involved. The mechanisms are complex but there is now strong evidence that differences exist for sizing by the dispersed size as opposed to saponified rosins (27). High pH's, lead to the size being either poorly retained or retained in an inappropriate state and thus to complete loss of sizing. This restricted the use of rosin alum sizing for many years to a pH of generally less than 6, and it is usually carried out at a pH of 4-5. The pH limitations exist

because of the acidic nature of aluminium sulfate in water. The aluminium ion in aqueous solution exists initially as a hexahydrated complex which is capable of further dissociation according to the equilibria shown in equations 4-6. Further equilibria are possible and the reader is referred to other texts on the chemistry of aluminium sulfate in water (28-32).

Equation 4	H+	+	[Al(H ₂ O) ₅ OH] ²⁺		[Al(H ₂ O) ₆] ³⁺
Equation 5	H+	+	[Al(H ₂ O) ₄ (OH) ₂] ⁺		[Al(H ₂ O) ₅ OH] ²⁺
Equation 6	H+	+	[Al(H ₂ O) ₃ (OH) ₃]		[AI(H ₂ O) ₄ (OH) ₂]

The extent of aluminium hydrolysis is an important factor in rosin sizing and also in wet end retention $(\underline{33})$. Alum is not the only metal salt which is able to act as a mordant. Ferrous and ferric ion have also been shown to be effective but none of these has yet found commercial use $(\underline{34})$.

The first stage in acid rosin sizing, as in all internal sizing is the retention of the size molecule in the fibre network during sheet formation. In the case of soap sizing this happens through the formation within the fibre suspension of an insoluble complex of poorly defined composition (known as aluminium resinate or the rosin-alum complex) which is then retained by a heterocoagulation mechanism. The rosin acids are to some extent bound co-ordinately to the aluminium in the complex, which has been shown to contain up to 100 Al-O units (35). Using isotopically labelled abietic acid, the aluminium resinate complex has been shown to be cationic in the pH range 4-6 and therefore probably retained by electrostatic attraction to the anionic fibre and fine surfaces (36-38).

Size retention is higher if aluminium resinate precipitation is performed at high stock consistency. However, this does not necessarily lead to the best distribution in the sheet and it has been shown that precipitation under dilute conditions leads to a more finely dispersed precipitate with a higher sizing efficiency (<u>37</u>). Increased pH or increased electrolyte concentration in the stock decreases the retention of size, and leads to poorer sizing. Electrolytes containing divalent ions also seem to be more detrimental than monovalent ions (<u>38</u>). These effects are consistent with a mechanism involving electrostatic interactions.

Soap and dispersed sizes have been shown to behave differently from each other in a number of respects, and a number of authors have suggested that different mechanisms were operative (26,39-42). This has since been confirmed (43-45). Whereas soluble soap size preferentially reacts first in solution with soluble aluminium ions, dispersed rosin acid reacts with aluminium species which have been pre-adsorbed onto the fibre surface. Optimum conditions for strong shear-resistant attachment are also different for soap and dispersed rosin sizing and are consistent with these different mechanisms.

Hydrodynamic and colloidal shear forces involved in fibre-particle interactions in the paper machine system have been shown to be important in the attachment of rosin size to fibre (<u>46</u>). pH, alum to size ratio, additives and addition sequence in the stock preparation system all affect the attachment of size. It is also important for soap size to maximise size distribution through the fibres before reaction with alum. This has been demonstrated on a commercial machine (<u>47</u>).

Fillers are well known to reduce rosin sizing efficiency in paper, and the effect of the filler seems to depend on the nature of the rosin size used. Dispersed acid size is more affected by fillers than soap size. Surface area and surface free energy differences do not explain satisfactorily the effects. The distribution of size has been measured by isotopic labelling, and the fillers have been shown to adsorb a substantial portion of size, but by way of multiple-layer surface coverage (48,49). The inefficiency of this adsorption process has been proposed as a possible cause of the adverse filler effect.

Hard water, and in particular of calcium ions make sizing considerably more difficult ($\underline{50-52}$). However, this may not be simply a retention effect. The role of both anions and cations in the retention mechanisms of both filler and sizing agent has been investigated. Both were shown to be retained over similar pH ranges, which coincide with that which corresponds to strong metal rosinate adsorption. However, anions were shown to have little effect upon rosinate adsorption, and hence have a correspondingly small effect on the retention of both the filler and the size ($\underline{53}$).

A number of authors have addressed electrokinetic aspects of internal rosin sizing (54,55). Dissolved anionic wood polymer extractives such as pine xylan or lignosulphonic acid increase the rate of liquid penetration in the paper. The penetration rate can be reduced by further addition of alum or cationic polymer,

and the negative influence of these anionic substances can also be reduced by using a pre-precipitated rosin (55).

In common with most other internal sizing systems, the heat treatment of rosin sized sheets (curing) enhances sizing $(\underline{56})$.

For reasons discussed earlier, it has now become more necessary to use rosin sizing at neutral pH. These methods require specialised modifications such as the selective addition of aluminium sulfate or the use of aluminium chloride or polyaluminium chloride (PAC). This subject is now discussed in more detail.

Neutral rosin sizing

It has been difficult to use rosin as a sizing agent under anything other than acid conditions due to the inherent acidity of aluminium sulfate solutions previously discussed. However, neutral pH rosin sizing has now become possible by a number of approaches. These include one or more of the following : the esterification of rosin for improved performance at neutral pH, the substitution of PAC for aluminium sulfate, the preparation of cationically stabilised rosin dispersions, and the premixing rosin with either alum or PAC.

Partial esterification of rosin facilitates its use at neutral pH, and rosin has been modified with monohydroxy alcohols such as ethylene glycol before modification with maleic anhydride. Sizes can then be prepared by saponification with sodium hydroxide solution, and are characterised by high sizing efficiency at neutral or close to neutral pH conditions (57). The best results are obtained with rosin which is partly esterified with lower alcohols (especially isooctanol) used in conjunction with small amounts of aluminium sulfate at a pH of 6-7. The esterified products also have some influence on various other properties of the modified rosin and paper sizes (58).

Esterification also seems to improve the stability of rosin emulsions. Emulsion particles of rosin acid size are unstable under alkaline conditions, but those of rosinglycerol ester-containing size have been found to be more stable. Polyaluminium silicate sulfate can also be used in place of alum to give better sizing. The aluminium compounds in the sheet appear to play a significant role in enhancing sizing characteristics without forming rosin-aluminium complexes (59).

The second approach commonly used in neutral pH rosin sizing is to replace alum with polyaluminium chloride. Like alum, PAC is able to bind rosin size and also to act as retention aid and coagulant for anionic trash, but it has the important advantage of not decreasing the pH as much as alum and also of being cationic even at neutral pH (<u>60</u>). Novel application techniques and good system control are very important if the formation of aluminium hydroxide is to be avoided (<u>61</u>). The rosin and PAC are also often pre-mixed prior to wet-end introduction, and results can be improved by using a cationic promoter and/or a retention aid (<u>62</u>). Whereas alum hydrolyses in situ, PAC is a prehydrolysed aluminium salt and does not show any tendency to form aluminium aggregates. Also the counter ion is a chloride ion whereas in alum it is a sulfate ion (<u>63</u>). Fine paper, sack paper, and carton board have all been successfully sized in the pH range 5.8-6.8. by this procedure (<u>64</u>). When used at a pH of 7.5 handsheets were found to have a higher breaking length and folding endurance than those made with conventional acid sizing systems (<u>65</u>).

A number of general articles on the use of polyaluminium chlorides with rosin for neutral sizing have been published (66-71) but little good mechanistic information is available. Polyaluminium chloride is a generic name given to a series of polymeric aluminium chlorides in which hydroxyl ions are substituted for some of the chloride ions. It is also known as aluminium chlorohydroxide, aluminium hydroxide chloride and polyaluminium hydroxychloride. It is not chemically stable when diluted (72) which can cause problems. It is prepared in a number of ways. Aluminium chloride can be hydrolysed with a base such as NaOH, Na, CO,, NH₄OH or lime. Alternatively HCl can be reacted with aluminium hydroxide at high pressure (71-73). PAC's have the general formula Al_n(OH)_mCl_{3nm}, and their degree of polymerisation varies and is a function of the hydroxyl concentration. In many ways the chemistry of solutions of aluminium chloride is similar to that of aluminium sulfate. Both form the octahedral hexahydrated complex aluminium ion, $[Al(H_2O)_{\ell}]^{3+}$, in solution in which six water molecules are co-ordinated to the aluminium ion. This complex is highly sensitive to pH and will form polymeric ions of the general formula given above, the simplest of which is the dimer, [Al₂(OH)₂(H₂O)₈]⁴⁺ but, in the case of aluminium chloride these polyaluminium species remain soluble and retain their cationic charge over a wider pH range than aluminium sulfate. The PAC's are characterised by their aluminium to chlorine ratio or, alternatively, by their basicity. The latter is defined as follows:

$$\%Basicity = \frac{100[OH^{-}]}{3[Al^{3+}]}$$

Where [OH] and $[Al^{3+}]$ are the total molar concentrations of hydroxide and aluminium ions respectively.

As basicity increases, the degree of polymerisation and the cationic charge of the polynuclear species also increases. However, the charge density, as expressed by the number of charges per aluminium atom, decreases. PAC's with basicities between 30 and 50% have been found to be effective and to give the ideal distribution of polynuclear aluminium species ($\underline{60}$). In addition to their use in neutral pH sizing, these highly charged polynuclear aluminium species are effective as retention and drainage aids.

Polyaluminium chlorides are generally used with dispersed rosin sizes which do not dissociate significantly at neutral pH ($\underline{71}$). Many variations in the use of PAC have been proposed but a common approach is the simultaneous addition of dispersed free rosin and PAC to the stuff box, cationic starch to the stuff box recirculation line, precipitated calcium carbonate to the fan pump and the use of an anionic retention aid (<u>60</u>). Levels of addition have been reported to be around 0.2-0.3% rosin (based on fibre) and 1-1.2% of the as-received polyaluminium chloride product (<u>60,71</u>) and sizing values of between 30 and 80 seconds HST have been obtained (<u>71</u>).

By careful use of alum it has been shown that it too can be used for neutral rosin sizing. This is done by pre-mixing the alum and rosin so that better control of pH in the neutral region can be achieved, and there are now many instances of such strategies being used (72). Fine papers and white top sheet have been sized in this (74, 75). Mixtures of aluminate and aluminium sulfate have also found some success in neutral pH rosin sizing (76).

Casein stabilised dispersions of rosin are anionic and therefore require a cationic mordant such as alum or PAC for effective retention by fibres. A different approach which has been applied to the neutral pH problem has been to make the emulsions in a cationically stabilised form, which may then be used at lower alum and PAC levels. This can be done in a variety of ways. For example, cationically dispersed rosin size can be prepared by adding a suitable cationizer to the anionically dispersed rosin size emulsion. Good stability can be obtained and the zeta potential of such emulsions has been reported to be around + 25mV. Sizing can then be performed at a pH of 6-8 without any precipitating agent, and the efficiency has been found to be about twice that of soap size. Handsheets have also been shown to be stronger (77). Other workers confirm that these require reduced

alum, and also that the possibility of interaction with filler is reduced (78). It has also been reported that there is less tendency to form sticky deposits with these sizes when calcium carbonate is present (79). The lower level of rosin required to achieve sizing and the reduced alum usage lead to a reduction in sizing costs. There is also evidence of reduced corrosion over the long term on the paper machine (80).

Some of the stabilising cationic polymers used in these systems (polyethyleneimine, polyacrylamide, egg albumen, poly (1,1-dimethyl-3,5dimethylene piperidinium chloride), diethylenetriamine, and polylysine) have been examined. Of the polyamines, polyallylamine was found to be the most effective at all pH's ($\underline{81}$). In the case of polyacrylamides, a small addition has been shown to provide a large level of sizing improvement when alum or cationic starch were also used. Higher charge densities gave better sizing, presumably due to increased retention, but molecular weight had little effect on sizing ($\underline{82}$). In the case of the polyethyleneimines, there is also evidence that, when metal ions are used with them, there is enhanced bonding between the rosin and the fibres ($\underline{83}$).

Aluminium-based microparticulate systems have also been used to good effect as a retention aid in combination with anionic dispersion size in wood-free fine paper stock containing calcium carbonate filler ($\underline{84}$). The sizing of fine papers with low calcium carbonate filler levels has also been shown to be commercially viable using these types of sizes ($\underline{85}$).

Other developments in rosin sizing

Synthetic anionic polymers have been tried for the emulsification of rosin, and these have shown better mechanical, chemical and freeze-thaw stability. They also give rise to less foaming and exhibit better sizing efficiency than conventional emulsions ($\underline{86}$).

In pulps which already contain residual rosin such as mechanical pulps and acid sulfite pulps (where rosin is incompletely dissolved) it is possible for sizing to be developed simply by heating the pulp. The effect, which is not always desirable, is known as self sizing. Alum, as might be expected, has a strong influence on self-sizing. Alum-free newsprint, for example, does not self-size appreciably but can be made to self-size by immersion in an acidic alum solution followed by drying at room temperature and to self-size completely after accelerated ageing at 105 ° C. This has made possible a simple method for sizing paper which contains

mechanical pulp, when alum is not in use at the wet end ($\underline{87}$). Buffering the alum-containing newsprint to pH 8 was found to have no effect on its tendency to self-size. Aluminium added by immersion in a suspension of aluminium hydroxide, however, did not induce self-sizing, and these results suggest that the role of alum in self-sizing is similar to that in conventional rosin-alum sizing.

It is important that the level of sizing in a product remains constant after its manufacture, and it has been found that the outer layers of reels of rosin sized paper show a greater level of sizing than the inner layers. The phenomenon has been ascribed to sizing migration (88,89).

Sizing with hydrophobic organic acids and alum need not be restricted to rosin and there are a number of examples of other acids which have shown good sizing behaviour These include saponified alkenyl succinic acids (90,91), diaryl acetic, proprionic and benzoic acids (92,93) and alpha hydroxy stearic acids (94).

In the case of saponified alkenyl succinic acid made from isoalkenes and maleic anhydrides (see also ASA) good sizing can be obtained and the main properties which have been found to influence retention are alum addition level and stock consistency. An alum level of at least 1.0%, a pH of less than 5.5, and precipitation in thick and low temperature stock produces the best results. The pH appears to affect the size precipitate and the stock temperature affects the degree of size coagulation (90,91).

Of the diarylacetic acids, diarylpropionic acids, and benzylbenzoic acids, acids containing an isopropyl group show the best sizing properties, and their sizing capacity increases with the number of methyl groups in the molecule. Dimethyl-xylylpropionic acid has in fact been found to be a better sizing agent than rosin. The acid can be synthesised by the condensation of isonitrosoacetone or pyruvic acid nitrile with m-xylene in the presence of sulfuric acid, yielding the oxime of dimethyl xylylpropionic aldehyde or dimethyl xylylpropionic acid nitrile. The oxime is converted to the nitrile by dehydration, and saponification of the nitrile yields dimethyl xylylpropionic acid (92). It is prepared for sizing in the same way as rosin size, by saponification and dilution, and is then precipitated with alum. Comparative sizing tests with pine gum rosin size showed that a high degree of sizing, comparable to that with rosin, could be obtained at 1% addition (93).

The alpha hydroxy carboxylic acids, in particular alpha hydroxy stearic acid, give good sizing when used in conjunction with alum. They are effective over a wide pH range and do not require curing in order to develop the sizing effect (94).

ALKYL KETENE DIMER SIZING

Synthetic Development

Alkyl ketene dimer sizing agents were a direct development of basic research carried out in the 1940's (95) which demonstrated that the parent molecule, diketene could derivitise hydroxyl groups, in particular those of cellulose. Their selection as potential sizing agents for cellulose seems to be based on the work of Staudinger and Eicher in 1952 (96) who used diketene to acetoacetylate cotton in glacial acetic acid using a sodium acetate catalyst. Kirillova and Padchenko (97) later extended this work to a range of conditions and catalysts. However, these non-aqueous conditions are very different from those used in the paper-making process, and the reaction cannot be assumed to occur so readily in an aqueous system. Reactivity is discussed more fully later. In 1947, Sauer (98) synthesised the first alkyl ketene dimer thus paving the way for Downey (99) in 1953 to develop the first alkyl ketene dimer containing long chain hydrocarbon alkyl groups for use in paper sizing. This work appeared in the patent literature in 1953 (99) and later (1956) in the open literature (100)

From considerations of the reactivity of the lactone ring, the dimers would be expected to form a direct covalent linkage with cellulose via β -keto ester formation. However, the molecule is also hydrolysed by water leading to a β keto acid which spontaneously decarboxylates to form a ketone. The ketone is then incapable of covalent reaction with cellulose. The general mechanism for this and the competitive hydrolysis reaction is shown in figure 4.



Figure 4

Emulsion preparation and retention

Commercial AKD's are prepared from long chain saturated fatty acids via the acid chloride. The synthesis involves the elimination of hydrogen chloride from the acid chloride to form an alkyl ketene monomer. This subsequently dimerises to AKD (equation 7):



Equation 7

The linear saturated AKD's are waxy, water insoluble solids with a melting point around 50°C whereas those from unsaturated or branched acids are liquids at room temperature. They are prepared as a stabilised emulsion by dispersion in a cationic polymer (normally cationic starch). They may vary from slightly to highly cationic with a dry solids content usually in the range 6% to about 15%. Typically around 30% of these solids would be made up of AKD and the remainder of cationic polymer. Small amounts of retention aids and surfactants may also be present. Particle size distributions are in the range 1-5u, and addition levels are normally around 1-2% of the as-received emulsion based on fibre. This is equivalent to a level of 0.05-0.1% of pure AKD based on fibre and is considerably lower than the amount of rosin used in rosin-alum sizing (1-2%). However it is more expensive than rosin, and comparisons should be made in terms of cost. Emulsions are fairly stable and show little hydrolysis even after several weeks. They can therefore be delivered to the paper production site by tanker as a pre-prepared emulsion and stored for several weeks if necessary before use. This obviates the need for on-site emulsification which is necessary for ASA sizes because of their greater hydrolytic instability

The first step in sizing is to retain the emulsified AKD particle in the wet web. The mechanism of retention is believed to be by heterocoagulation of the cationic size particles to the negatively charged fibre surface (<u>101</u>). The charge characteristics of the stabilising polymer become important as demonstrated by the effect of pH on the retention of AKD emulsion particles stabilised with a tertiary cationic starch (Figure 5).

There is a decrease in electrophoretic mobility of the AKD particle as the pH is increased, which is consistent with deprotonation of the charged tertiary amino cationic group at high pH. The charge of bleached kraft pulp is also shown in figure 5, and at pH's below 4, it becomes less negative due to the reversal of dissociation of acidic groups on the fibre surface. The optimum charge difference is found between pH 5 and 7 which suggests that optimum retention would be expected at around neutral pH, and this has been found to be the case (102,103). The nature of the charge of which is largely independent of pH, would not be expected to display the same decrease in mobility at high pH.



Figure 5

There is evidence that the emulsion stabilising polymers are involved in dynamic transfer processes in a manner similar to retention aids. It has been shown that there is a transfer of retention polymers among the particles in the paper machine wet end and also a transfer of alum and AKD from fibres to fillers. These are believed to have important practical consequences (104).

The stabilising polymer also appears to influence the rate of development of sizing (cure rate) after the sheet has been made (105). There is evidence that they assist both reaction and cure though the two processes are considered to be independent of each other. Polyamines and polyamides have been shown to encourage both reaction and cure, polyamines giving better results with cure.

Sizing efficiency has also been shown to be dependent upon the chain length of the hydrocarbon groups. As the carbon number of the hydrocarbon chain increases from C8 to C14, sizing efficiency increases. It then levels off with only minor variations up to C20 (106). There is a wide diversity in emulsion technology, and

AKD emulsions are now available which are designed to meet the requirements of different paper and board products and machine speeds (107,108)

One of the more interesting approaches to emulsion preparation and retention has been the addition of AKD-modified fibres to a furnish (109). In this method, as little as 5% of pre-treated fibres which have been impregnated with AKD have been shown to give good sizing when added to a papermaking furnish. The main advantage of such a method is that it should be possible to achieve very high retention of the AKD-modified fibres in the sheet and hence to give more cost-effective use of the size. From past studies on the migration of AKD, it would not be surprising if such a method was successful and it is likely that its success is due to the migration and subsequent reaction of the AKD from the impregnated fibres during drying.

Emulsion and hydrolytic stability

The stability of size emulsions is a very important commercial and practical consideration, both in terms of their resistance to hydrolysis and also in terms of the colloidal stability of the dispersion to aggregation and sedimenation. Although AKD emulsions are stable to hydrolysis for quite long periods, there has been little study into the effect, if any, that hydrolysis has on emulsion stability. The mechanism of deterioration of alkylketene dimer (AKD) emulsions during storage at 4°C has been studied in terms of hydrolysis of AKD, deterioration of the emulsion stabiliser, and crystallisation of AKD. The dispersibility and homogeneity of AKD emulsions have been shown to be significant factors in AKD sizing. It has been proposed that in partly hydrolysed AKD emulsions which contain 10-25% ketones the ketones on the surface of the emulsion particle are responsible for the decrease in dispersibility and poorer sizing efficiency of the emulsions (110). However, emulsions of mixtures of AKD and hydrolysed AKD are able to size even when 75% hydrolysed AKD is present. The presence of unhydrolysed AKD seems to be necessary if a homogeneous distribution is to be formed (111).

Reactivity

Diketene and alkyl ketene dimer derivatives have been shown to be surprisingly unreactive towards water and hydroxyl containing compounds even in homogenous solution at relatively high temperatures (<u>112</u>). The general reactivity of the higher analogues of diketene, the alkyl ketene dimers, would be expected to be lower than that of diketene because of the steric crowding of the reactive

lactone ring by the two long chain alkyl groups. This has indeed been found to be the case for tetradecyl ketene dimer (103). The rate of its hydrolysis and also its reaction with alcohols at neutral pH is very slow but, under basic conditions, it is much more rapid. The authors suggest that reaction between alkyl ketene dimers and cellulose in the papermaking system is likely to be slow, and in particular it is likely to be slower than the competitive hydrolysis with water.

Machine temperature and pH are both important variables. High temperatures and pH have been shown to accelerate both the rate of hydrolysis and of esterification (<u>113,114</u>). Marton (<u>113</u>) studied the kinetics of cure and hydrolysis and, using the activation energies, concluded that the rate of hydrolysis to form the ketone would be significant at the high temperatures experienced during drying. Marton also further demonstrated (<u>113,114</u>) that the ketone hydrolysis product exhibited little sizing. This confirmed the work previously reported by Garner (<u>102</u>) and has, more recently, been supported by Yajun (<u>115,116</u>).

Evidence for direct B-keto ester formation with cellulose has been difficult to obtain. The early literature shows that the dimer appeared not to be extracted by organic solvents and that, on treatment of the dimer-sized fibres with cuprammonium solution (a solvent for cellulose), an insoluble shell remained. This was presumed to be the reacted external surface of the fibre (100). Research with ¹⁴C labelled dimers (117-121) has shown that, although some of the dimer is irreversibly bound to the fibres, varying amounts of the unreacted dimer can, in fact, always be extracted. The existence and extent of any reaction has therefore been somewhat controversial, and attempts have been made to demonstrate B-keto ester formation by FTIR spectroscopy (122-126). Pisa and Murkova (122) and Rohringer (124), using multiple internal reflectance infra red spectra of sheets of paper sized with alkyl ketene dimers, were unable to detect the characteristic infra red bands associated with the unreacted dimer. Lindstrom (123), however, claims evidence for a \beta-keto ester linkage using similar methods and Odberg and Lindstrom (125) report that a band at 1745 cm⁻¹ was observable in solvent extracted sheets which had been treated with AKD and cured. This band was assigned to the ester carbonyl of the β -keto ester of cellulose. That a reaction can be made to occur between cellulose and AKD has been demonstrated by Nahm (127) using dimethylformamide as a solvent. However, it is difficult to draw any conclusions about reactivity from this work, as the conditions are very different from those of normal papermaking.

The most persuasive evidence for the formation of an AKD-cellulose β -keto ester has been obtained using ¹³C labelling and solid state nuclear magnetic resonance spectroscopy (<u>128,129</u>). The work also shows that the AKD associated with calcium carbonate fillers transforms to ketone hydrolysis product over time

However, there is still controversy in this area and other workers have suggested an alternative mechanism. By extracting AKD and its related compound from AKD-sized sheets under various conditions and chemically analysing enzymatically-hydrolysed residues of AKD-sized sheets and cured mixtures of amorphous cellulose and AKD, it has been suggested that AKD and ketones (hydrolysed AKD) were most likely to be trapped in sheets without the formation of β -ketoesters. Defibration of AKD-sized sheets and swelling of pulp fibres were found to be necessary for complete extraction of AKD and ketones (130). Also cellulase enzymatic treatment of AKD sized sheets and subsequent analysis by gas chromatography, Fourier transform infra red spectroscopy, and nuclear magnetic resonance spectroscopy has been used to show that the AKD was present in the sheet as either AKD or ketone (131).

More controversially, Gess (132,133), proposes that all sizes can undergo reactions leading to the formation of either strong or weak bonds - the so-called strong bond/ weak bond theory. AKD is proposed as a predominately weak bond size, the majority of bonds being labile and broken in the dryer section allowing the AKD to migrate and deposit in the dryer hood of the paper machine. The theory has also been applied to rosin-alum sizing where it is proposed that strong bond and weak bond complexes are formed and that only the rosin in a weak bond complex undergoes redistribution when the paper sheet is dried (132).

Gess's explanation seems to be unnecessarily complicated and it is probably more correct to conclude that the deposits found in dryer hoods arise from the vapour phase migration of unreacted AKD from the sheet. Vapour phase migration of AKD has been observed by Akpabio and Roberts (134) but, at high humidities, they observed some hydrolysis of the dimer. This, in itself, does not preclude the possibility that at least some of the AKD has undergone reaction with the fibres. At the moment, therefore, β -keto ester formation still appears to be the most probable mechanism by which sizing is induced.

Isotopic (14 C) labelling techniques have proved to be a powerful tool for investigating the reactivity of the dimers towards cellulose and water in paper prepared under standard handsheet conditions (<u>117-121</u>). These techniques have

demonstrated that heat treatment is essential for reaction between the dimer and the fibre to take place and for the development of sizing (<u>117,119</u>). Figure 6 demonstrates the importance of heat treatment. Furthermore, the more severe the heat treatment the lower is the level of retained dimer which is necessary to induce good sizing. This is probably a distribution effect, and support for this has been obtained by autoradiography of sheets sized with ¹⁴C labelled AKD. This shows that diffusion and migration occur as a result of heating (<u>103</u>).



Figure 6

The degree to which the dimer has become irreversibly 'bound' or reacted with the cellulose has been studied by solvent extraction methods (<u>117-121</u>). Sheets which had been sized with labelled compounds then dried by different methods were extracted with a solvent capable of removing the unreacted AKD. Lindstrom (<u>118</u>) was able to show that the small amount of AKD required to give a COBB₆₀ of 25 g m⁻², after removal of unreacted dimer by solvent extraction (0.008 to 0.038%), showed a strong correlation with the BET-surface areas of the pulps used (figure 7). Using these results together with surface balance measurements, a surface coverage of 4% of planar oriented monolayer was calculated to be necessary to give this level of sizing.



Figure 7

It was also further demonstrated $(\underline{118})$ that, for a bleached kraft softwood pulp, a threshold amount of reacted AKD was necessary to give good sizing and that once that threshold had been exceeded, a large increase in sizing developed for only small increases in reacted AKD (figure 8)



Figure 8

This very sharp increase in sizing over a narrow range of size addition is very typical of all internal sizes and explains why sizing determination in these ranges is often difficult to reproduce.

Material balances for alkyl ketene dimer (AKD) and its hydrolysis products have been determined for commercial production runs. AKD retention was found to be in the range 69 to 95%. Of the total retained AKD only 20-38% was found to be usefully reacted, the rest being affected by hydrolytic side reactions (<u>135</u>).

The crystallisation and coagulation behaviour of AKD and hydrolysed AKD in sheets after melting has also been shown to have an effect on sizing. Hydrophilic compounds with a lower crystallisation or coagulation point produce sheets with better sizing. N-hexane or water vapour treatment of AKD-sized sheets also improves sizing behaviour. Some of these changes are attributed to changes in the orientation of alkyl chains (<u>136</u>).

Size promotion

One of the most important features of AKD sizing is that the development of sizing is slow and takes place after drying and during reel-up. It has been shown that sizing development may take place over a period as long as 10 days (figure 9) and that the ultimate sizing level is a function of the drier temperature (137). Higher storage temperatures were also found to have a large effect upon the rate of sizing development. Greater levels of reaction were observed to occur during storage.



Figure 9

Because of this slow rate of reaction, catalysis has also been studied. HCO_3^{-1} ions and polyamideamine-epichlorohydrin resin have been shown to exert a strong catalytic effect (<u>121</u>). A speculative trimolecular mechanism for the catalytic effect of HCO_3^{-1} ions has been proposed (<u>121</u>).

The development of faster curing AKD sizes has since been reported (138). Specifically designed cationic polymers have been incorporated into the AKD emulsion preparation as promoters to improve sizing efficiency and cure rate. Little detail is available in the basic research literature on the mechanism by which such additives impart improvements, and it has not yet been established with certainty whether these promoters improve the retention of the dimer or improve the cellulose reaction kinetics. Some practical studies have been carried out in which the chemical environment has been varied and promoter-free and promoter-containing AKD's have been used. The most effective combination was found to be promoter-free AKD's with modified polyethylene imine and an anionic polyacrylamide as the retention aid system (139). A study on a commercial paper machine system using a waste stock of the effects of a variety of cure promoters showed that cure rates improved to different degrees. The improvement seemed not to be caused by improved fines retention or by AKD distribution between fibre and fines (140).

The enhancement of efficiency caused by polyamide polyamine epichlorohydrin resins is also influenced by viscosity and degree of polymerisation. When a polymer with a viscosity of 39.6 mPas at 25 °C at a 10% solids content was used the surface absorbency of the sized hand sheet showed a dramatic decrease at an addition level of 0.01-0.05% polymer on pulp (<u>141</u>). This was ascribed to the increased viscosity preventing molecular chains from cross-linking.

One of the disadvantages of these cationic polymer cure promoters is that they tend to decrease the efficiency of optical brightening agents (OBA's) (<u>142</u>). This is known as quenching of OBA. However, AKD used in conjunction with a highly cationic starch as a hydrocolloid component has been found to decrease size and OBA consumption and to eliminate toner problems whilst maintaining runnability (<u>143</u>).

Alum is not necessary in AKD systems but may be beneficial when used at low levels. Some studies into the effect of alum on sizing in AKD systems have been made (<u>144-146</u>). Akpabio and Roberts (<u>144</u>) observed a decrease in sizing efficiency when AKD was used in the presence of high levels of alum, and they

concluded that this was not a pH effect but could be attributed to interference of the AKD - cellulose interaction by adsorbed aluminium species. Alum has also been reported to increase hydrolysis in the pulp slurry (<u>146</u>) and this may also account to some extent for the decreased effectiveness of AKD in the presence of alum. Wortley (<u>145</u>), on the other hand, reports that it is possible, by careful application, to use alum at lower levels effectively in alkaline AKD systems and, under these conditions, improved sizing can be obtained.

Size reversion

AKD and ASA sized papers sometimes have a tendency to lose their sizing with time, an effect which has come to be known as sizing reversion. The effect seems to be particularly common in papers containing precipitated calcium carbonate fillers. A wide range of PCC fillers are able to cause reversion and the degree of reversion increases with filler amount (<u>147</u>). Increasing the paper drying temperature for filled paper has the effect of reducing the initial sizing, in contrast to unfilled paper (<u>112</u>), but the effect is less severe when larger particle sized PCC's with lower specific areas are used. There appears to be a maximum size of PCC particle beyond which no further effect on sizing performance or reversion is observed (<u>148</u>).

No completely satisfactory explanation for this effect is currently available. However it has been suggested that reversion may be due to environmentally induced molecular reorganisation of the AKD-modified fibre surfaces thereby changing the surface energy of the alkyl chains of the AKD and resulting in reduced water repellency (149). An alternative mechanism which has been suggested is that there is transformation of AKD associated with calcium carbonate fillers to ketone hydrolysis product over time (128).

Practical considerations

A number of process variables influence AKD sizing, the most important of which are probably pH and drying conditions. However, pulp type, fillers, addition point and the presence of wet-end chemicals have also been reported to be important (150). In addition, sizing efficiency has been shown to be affected not only by the amount of size added, retained and reacted, but also by the retention of fines and filler (151).

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It is common to dry sheets to very low moisture contents before the size press (typically 3-5% but sometimes as low as 1-3%). This assists greatly but, even under these conditions, there is still considerable off-machine development of sizing (106). It is necessary therefore to assess the ultimate level of sizing that may be produced by carrying out some form of off-machine cure test, and this is commonly done. However, it is necessarily somewhat uncertain as a method of evaluating ultimate sizing. AKD sizes are generally used over a pH range of 6 to 9, but are more effective at the higher end of this range (106). High pH generally increases the rate of reaction but it would also be expected to accelerate the rate of hydrolysis of the β -keto ester of cellulose. Size reversion may therefore become a more serious problem at high pH.

Pulp type is also important and, in general, unbleached pulps are easier to size than bleached pulps. High α -cellulose pulps are extremely difficult to size and require as much as 10 times the amount of reacted AKD to produce similar levels of sizing to those of Kraft pulps (<u>106</u>). This effect cannot be explained in terms of surface area.

As in rosin sizing, the presence of fillers usually increases the amount of AKD required. Reaction with filler surfaces is not theoretically possible and sizing is probably bought about by the unreacted AKD. As this is much less efficient than the well-oriented esterified AKD, a proportionally greater amount of size may therefore be needed. Despite this, economic benefits have been demonstrated when calcium carbonate is used as a filler, particularly if preliminary flocculation of the carbonate is employed (152). Filler morphology also seems to be important and, in the case of precipitated calcium carbonate, it has been shown that the use of 1:1 mixtures of scalenohedral and prismatic PCCs will allow filler loadings to be increased from 18 to 24 % without a significant increase in AKD usage (153).

ALKENYL SUCCINIC ANHYDRIDES

Synthetic development

The development of alkenyl succinic anhydrides as sizing agents came later than the AKD's and took place in 1974 (<u>154</u>). Like AKD's they are able to undergo reaction with cellulose and water and the reaction paths are shown in figure 10. The ASA's are considerably more reactive than the AKD's and can promote sizing without heat treatment (<u>155</u>).



(R = C₁₄ C₁₈ unsaturated) Cellulose-OH H R - C - COOH H - C - C - O - cellulose H O

Figure 10

Unlike the AKD's, which are derived from fatty acids, the ASA's are derived from petrochemical feedstock (1-alkenes or α -olefins). This has implications for their economics, particularly during times of high oil prices. They are prepared from α -olefins by catalytic isomerisation (<u>156</u>), followed by an addition reaction with maleic anhydride (the ene reaction). The reaction scheme is shown in figure 11. A full discussion of the stereochemistry and mechanism of this reaction is beyond the scope of this review but is available elsewhere (<u>157,158</u>). The location of the double bond in the alkene is important and it has been shown that the internal alkenes are much more effective than α -olefins, being solids at room temperature, require higher temperatures for emulsification than the isomerised ASA's derived from isomerised olefins. This is likely to accelerate rapidly the unwanted hydrolysis of the size.

It has been possible, using ¹⁴C radiolabelled C12 and C18 α -olefins and their catalytically isomerised derivatives, to confirm that α -olefins are more readily hydrolysed than isomerised forms. At longer chain lengths, the isomerised form is also slightly less reactive towards cellulose than the α form but promotes a higher level of sizing per reacted molecule. An explanation has been proposed in terms of the more effective shielding by the alpha form of the carboxyl group introduced during monoesterification (160).



Figure 11

Emulsification

Anhydrides made from isomerised α -olefins with a carbon number of C16-C18 are usually used commercially. Olefins with a carbon number lower than C14 tend to give anhydrides which are less effective (<u>159</u>) and ASA's prepared from olefins with a carbon number of more than C20 are solids at room temperature and are therefore less suitable for emulsification. It has been suggested that the most effective hydrocarbon chain length is 18 (<u>161</u>) and this has been confirmed in more recent work (<u>160</u>).

Emulsions are usually prepared using cationic starch as the stabilising polymer. Starch concentrations in the emulsions are usually in the range 1-2%, and the ratio of starch to ASA is generally around 3:1. Starch characteristics are known to influence ASA sizing, and it has been shown that sizing is enhanced by a high cationic charge and by a high starch addition level. However, the starch molecular

weight appears not to be a significant factor (162). It has also been observed that starches with relatively high levels of bound phosphate (>0.5%), although beneficial to filler retention, cause substantial decreases in both ASA and AKD sizing (163).

Because of the relatively rapid rate of hydrolysis, emulsification has to be carried out on-site using either a low-shear venturi system or a high-shear turbine system. In the former, a surfactant activator (usually around 5% based on ASA) is often used, although excessive use of the activator is thought to be detrimental to sizing. In the high shear turbine system, less activator (typically around 1% based on ASA) is used. Regular maintenance of the system is required (typically monthly) and it is usual to have a back-up system. Particle sizes in the range 1-2 μ are aimed for and these can usually be easily achieved.

Emulsion quality, in particular particle size, is very important. It can be measured by conventional light scattering techniques or, more simply, by turbidity (164), which has been shown to be primarily a function of emulsion particle size. A direct correlation exists between emulsion particle size and turbidity and between turbidity and sizing efficiency. In the low shear emulsification system it has also been shown that care must be taken in optimising the surfactant activator in order to obtain good ASA emulsion quality. Cationic starch functions not only as an emulsion stabiliser but also to some extent as a surfactant activator. Sizing increases are observed at high starch to ASA ratios and these may, in part, be due to a decrease in emulsion particle size.

Various attempts have been made to improve the emulsification technology over the past few years. Emulsions have been produced by turbine emulsification in a dilute aqueous solution of synthetic cationic polymer. This has been shown to give more stable emulsions with a smaller average particle size of around 0.5 μ than those obtained with cationic starch (<u>165</u>). Modern polymer technology has been applied to produce self-emusifying sizes which simply require to be mixed with water prior to use (<u>166</u>). This has the advantage of reducing the costs of on-site emulsification and reducing size losses through hydrolysis when the emulsion is left to stand. However, little widespread commercial use has been made of them.

Hydrolytic stability

The hydrolytic stability of ASA emulsions is very important in sizing efficiency and this has been studied by various workers (167-169). The rates of hydrolysis are



much faster than AKD and some typical results are shown in figure 12.



At an initial pH of around 7, and without pH adjustment, the hydrolysis would be complete in, typically, around 30 hours. The final pH of the emulsion being around 3.5 due to the formation of the weakly acidic dicarboxylic acid. The hydrolysis displays a short induction period followed by an accelerating rate. The acceleration is difficult to explain on the basis of particle size considerations, as the hydrolysis product is reasonably soluble in water at these concentrations and would be expected to be dissolved from the particle-water interface during hydrolysis. This would lead to a gradual decrease in the total surface area of the emulsion and to a decrease in the rate of hydrolvsis. It is also not possible to explain the acceleration in terms of an autocatalytic effect, for although anhydride hydrolysis can be both acid and base catalysed, acid catalysis requires a much lower pH and is insignificant at a pH of 3.5 (170,171). The most likely explanation seems to be in terms of the protective action of the starch molecule at the surface of the emulsified ASA particle which may act as a barrier to the transport of water to the particle surface. As water diffuses through this barrier, hydrolysis occurs, the emulsion becomes destabilised and the rate increases. An alternative explanation is that the hydrolysis product dissolves in the ASA particle and, in doing so assists in the transport of water into the particle interior, hence increasing the rate.

The hydrolytic stability of these ASA's in both homogeneous and heterogeneous (emulsion) solution has also been studied. In both cases the alpha form was more

quickly hydrolysed than the isomerised form, and this is in line with their reactivities towards cellulose. Emulsions of the C12 alpha form, however, displayed unusually high stability (160). Finally, there is some evidence that the addition of adipic acid to emulsions reduces the rate of hydrolysis (162).

Mechanistic Aspects

The main advantage of ASA is that it is very reactive, and full sizing develops immediately off the paper machine. Good first pass retention is essential to ensure optimum performance and machine cleanliness (<u>172</u>). The reactivity of the ASA has been confirmed by work with ¹⁴C labelled ASA which has shown that sizing can be induced merely by conditioning the sheets for 24 hours at 20°C and 50% RH, no heat treatment being necessary (<u>155</u>). This contrasts sharply with AKD sizing, in which sizing only develops after the sheet has been subjected to fairly extreme heat treatment (<u>103,117-121</u>). Even so, there is still some development of sizing off-machine. Sizing development has been shown to be dependent on the amount of ASA retained, pH, curing temperatures and conditioning time (<u>173</u>).

Various authors (173-176) have demonstrated that the dicarbxylic acid product of hydrolysis is inhibitory to sizing. Roberts and Wan Daud (155) also showed that solvent extraction of ASA-sized sheets usually led to an increase in sizing, and explained this in terms of the inhibitory effect of hydrolysed excess ASA. Confirmation of the de-sizing nature of the acid has since been obtained by performing an experiment in which sheets were sized with ASA at pH 7 and the unreacted and/or hydrolysed ASA extracted with chloroform (155). The amount of reacted ASA was 0.31 mg/g and the sheets had a HST value of 207 seconds. Dicarboxylic acid was then applied at different levels of addition by a solvent application procedure from toluene. A progressive decrease in sizing was observed which was a function of the amount of added acid (figure 13). However, the sizing could be completely restored to its original level by solvent extraction of the applied acid. It is probable that the dicarboxylic acid produced by hydrolysis is able to become adsorbed to previously reacted alkyl groups in a way which allows the orientation of its polar carboxyl groups away from the fibre surface and towards advancing water molecules.

This behaviour contrasts with that of AKD sizing, where no increase in sizing is observed after solvent extraction. In the case of AKD, the rate of hydrolysis is much slower, but there is also no evidence that the ketone produced by hydrolysis acts as a desizing agent (102).



Figure 13

The effect of pH on the degree of reaction and upon the sizing has been studied (<u>177</u>). Ink penetration times were shown to be highest at pH 7 and lowest at pH 11 for equivalent levels of retained ASA. The sizing at pH 4 was slightly lower than that at pH 7. These results were explained in terms of the competitive hydrolysis, which is considerably faster at pH 11 than at pH 7 and probably marginally faster at pH 4 than at pH 7.

It is likely that residual unreacted ASA in a sheet will slowly hydrolyse to its dicarboxylic acid and may then contribute a de-sizing effect. Optimum sizing in the ASA system is therefore likely to be achieved by maximising the level of reaction with cellulose and minimising the degree of hydrolysis. It is also likely that increasing the amount of ASA used beyond a certain threshold level will not be beneficial.

Practical considerations

The planning of a conversion to ASA sizing is a major operation and must be done in well-planned stages. The total chemistry of the wet-end additive system must be considered, ie filler, retention aid (charge and molecular weight), alum, biocides etc. Pre-conversion monitoring is also strongly recommended (178).

There are a number of practical considerations when using ASA as a size. Hydrolysis of the size, as has been discussed earlier, must be avoided. Emulsion storage time should therefore be minimised or eliminated. The ASA should also be added at a point which keeps contact time with the stock to a minimum. It is also important to retain as much of the size and also the fines, onto which much of the size is adsorbed, as possible in order to prevent recirculation of hydrolysed size around the whitewater system. Hydrolysed ASA in the whitewater system is well known to give pitch and deposit problems, probably as a result of formation of insoluble calcium and magnesium salts of the dicarboxylic acid hydrolysis product (179,180).

These insoluble salts have been implicated in press picking, but the introduction of aluminium ions in the form of around 0.5% alum has been shown to be an effective way of minimising or eliminating the problem (181). The tackiness of these soaps has been related to a number of variables such as pH, retained metal and the amount of free acid. In one mill, an ASA conversion was monitored continuously for two years after the initial change and a number of possible modifications to such things as the retention aid system, the use of double and triple forming fabrics were identified (182). A number of published experiences of mill operations and conversions and of pilot plant trials with ASA are also available (183-189).

As well as the prevention of deposits, small amounts of alum have been shown to be beneficial to sizing with ASA (<u>172</u>). An explanation for this behaviour has recently been put forward in terms of the cationic behaviour of alum under alkaline conditions (<u>190</u>). Even when the stock had been mixed for an extended period, the late addition of alum has been shown to improve sizing dramatically (<u>191</u>). It is proposed that, provided the contact time is kept short, the alum acts as a cationic donor.

SURFACE PROPERTIES AND PRINTABILITY PHENOMENA

There has been a considerable interest over the last few years in the surface characteristics of sized papers, particularly with regard to their printability, adhesion and converting performance. The surface energy of acid-base interactions in sized and unsized paper handsheets has been determined by both dynamic contact angle analysis (192), and by inverse gas chromatography (193). AKD and rosin/alum sizing were both shown to reduce the solid surface energy and the acid-base energy of adhesion (192).

The wettability of fibre surfaces treated with AKD has also been evaluated by determining the single fibre advancing contact angle of water (194,195). Sizing performance was found to be dependent both on sheet structure and wettability, and the single fibre contact angle was non-linearly proportional to the AKD dosage. Unreacted AKD was also found to make a contribution to the hydrophobicity of the fibre.

The distribution of alkyl ketenedimer (AKD) in hand sheets has been characterised using variable angle electron spectroscopy. The AKD has been found to cover only part of the cellulose surface, but sufficient sizing is achieved when 15% of the surface is covered (<u>196</u>).

Ink jet printability is particularly susceptible to the effects of sizing due to the method of ink placement and spreading on the sheet. It has been shown that, as fibre wettability decreases, sizing print quality increases. Sheets sized with increasing amounts of alkenyl succinic anhydride displayed a corresponding increase in print quality. However, when filler was added to the sheet, the degree of sizing of the sheet significantly decreased and the extent of wetting heterogeneity dramatically increased, both of which contributed to a decrease in print quality (197).

A number of printability studies have been carried out. The use of AKD and PCC containing paper has been shown to facilitate improved printability, and to give high levels of flexibility (<u>198</u>). AKD has been shown to enhance inkjet printing print quality and to give good colour definition, to decrease dusting and copier contaminant in copier paper (<u>199</u>). A combination of ASA and starch and styrene-acrylic resin surface size gave good print quality as measured by densitometry and image analysis (<u>200</u>). There is also now good evidence that that the combined effects of internal and external sizing both contribute towards printing performance (<u>201-203</u>).

Using electron spectroscopy, Borch and Miller ($\underline{204}$) studied size distribution on the surface of printing papers. They showed that there was an increase in the hydrophobicity of the surface of sized sheets and that this corresponded to a decrease in the oxygen to carbon ratio. The authors used this as a measure of sizing and were able to demonstrate that sizing was well distributed at the resolution level of the electrophotographic printing techniques.

Sizing is sometimes carried out by application at the size press. This is still relatively uncommon but is growing in popularity. The main difficulty to overcome is to achieve z- directional penetration. Sizing by this method is more likely to be restricted to the surface and it is often used in addition to wet-end sizing rather than in lieu of it.

There have been a number of studies into the effect sizes on the frictional properties of paper. There is some evidence that neutral sizes, and AKD in particular, tend to give rise to a more slippery sheet than rosin-alum sizing (113). Both ASA (205), and rosin (206), seem to perform better. This can have important implications for those converting operations which are susceptible to changes in frictional resistance. Marton (113) has demonstrated that the presence of dialkyl ketones derived from the hydrolysis of AKD on the surface of paper decreases the friction between contacting paper surfaces. Liquid AKD's have now been developed in response to this problem. These are AKD's which are liquids rather than waxes at room temperature and are prepared from either unsaturated fatty acids or from branched fatty acids. These seem to perform better in terms of slip than the higher melting point AKD's in such applications as envelopes, forms and reprographic paper and in precision-converting operations (207). There is also some evidence that AKD may assist in suppressing the capillary movement of aqueous adhesives when corrugated starch adhesive is used in board by reducing the extent of dehydration of the adhesive (208).

Problems can also occur through incompatibilities between surface energies of hydrophilic cellulose and non-polar polyolefins such as polyethylene and polypropylene. The decrease in surface energy of the paper surface brought about by AKD sizing has a detrimental effect upon polyethylene adhesion strength (209). It has also been shown that composite sheets formed between conventional pulp fibres and surface-modified polypropylene fibre show poor adhesion with the surface of polypropylene fibres (210).

Hot extended nips have been used as self sealing reaction vessels as an alternative to wet end sizing. ASA and AKD are redistributed by spraying on to one side of unsized paper prior to the nip. The hot press nip acts, for an extremely short period of time, as a closed pressure chamber with a reasonable degree of sealing. Chemical reactions, including gas phase reactions can occur under these conditions and it is possible to arrange for reactions to take place on one or both sides of the paper web. Three types of reaction have been proposed to take place either separately or together. These are redistribution and chemical anchoring of low molecular weight oleophilic components on the fibre surface, crosslinking of wood polymers, and changes in the web structure to give greater smoothness or a greater bonding area (211,212).

Finally, some improvements in brightness have been noted when AKD is used as a sizing agent (150).

MIXED SIZING SYSTEMS

There seems to be some advantage to be gained in some grades of paper by using mixed sizing systems. Liquid packaging board for aseptic packaging systems have to meet a rigorous high-temperature hydrogen peroxide edgewick specification and must also be resistant to lactic acid and other aggressive low surface energy penetrants. A combined sizing system of AKD and a cationic rosin size used in conjunction with alum gives a synergistic improvement when used in these types of board (213). No adequate explanation in mechanistic terms is, however, available for this apparent synergism.

Combinations of AKD and ASA when used in full or pilot scale production of fine paper containing precipitated calcium carbonate have also been shown to give a better sizing response, less size reversion, and allowed the use of higher filler levels with higher specific surface area. There was also less migration, higher frictional resistance and better ink jet printability (214).

SIZE TEST METHODS

Quite a large number of quantitative sizing tests are available, but the two which are in most common use are the Cobb test and the Hercules size test (HST). These tests measure the penetration of water or an aqueous ink through the z direction of the sheet. The Cobb test measures gravimetrically the amount of water in g/m^2 which penetrates in a fixed period of time (usually one minute) whereas the HST measures the time to achieve a predetermined degree of penetration as determined by the reflectance of the underside of the sheet. Correlation between the two tests is often poor, and this is not surprising as they measure different properties of the penetration-time relationship. Sheet grammage is also an important factor, having little influence in theory on the Cobb test but a significant effect upon HST at high grammage. It is not uncommon therefore to find large differences in HST for

papers which have very similar Cobb values. Single fibre contact angle measurement, can also be used and has been shown to be more sensitive than either the HST or Cobb test (194).

Various inks have been used in the Hercules Size Test. The mordant in rosin-alum size is an aluminium co-ordinate complex and is readily attacked by acids, alkalis, and aluminium complexing ligands such as the fluoride ion. This affects the rate of ink penetration. In AKD sizing the β -keto ester bonds seem to be more resistant to this attack (215).

Dynamic sizing tests such as the Bristow absorption test shows that both wetting delay and absorption rate are affected strongly by sizing at low size addition levels. The method is also sensitive to two-sidedness (216).

COMPARISON BETWEEN SIZING SYSTEMS

The main difference between the two reactive sizes AKD and ASA is the lower reactivity of the AKD's. Whilst undesirable, this does have advantages in terms of the stability of the aqueous emulsion. AKD emulsions are stable towards hydrolysis for several months (102,106), which means that they can be delivered by tanker and stored for a reasonable period before use. ASA emulsions, on the other hand, have a very poor hydrolytic stability and must be prepared on-site immediately prior to use. In addition, the products of hydrolysis differ in their effects. The product of hydrolysis of AKD is a ketone which, although having a small positive sizing effect in its own right, is not as effective weight for weight as the covalently bound AKD (102). Excess unreacted AKD in the sheet, whilst undesirable, is not a particular problem as far as sizing is concerned. The hydrolysis product of ASA, on the other hand, has a seriously detrimental effect on sizing if it is retained in the sheet. This effectively limits the extent to which sizing can be achieved using ASA. Excess unreacted ASA will be hydrolysed by equilibrium moisture in the sheet, and attempts to increase sizing by increasing the level of addition of ASA may therefore be self-defeating.

The level of reaction which can be achieved with each of these sizing systems is therefore important, and this is a subject which has given rise to a certain amount of controversy in the literature (103,112,117-124). There are those who maintain that any reaction at all between cellulose and AKD is unlikely under papermaking conditions (112), and there are those who maintain that very high levels of reaction

can be obtained (<u>119</u>). Close scrutiny of the experimental methods and conditions, where available, shows that AKD is in fact very unreactive towards cellulose unless high pH and extreme drying temperatures and times are used (<u>102,103,115,117</u>). Most commercial papers made at pH's of around 7-8 will contain a significant proportion of unreacted AKD which will presumably eventually be converted into its ketone hydrolysis product. However, the reacted AKD gives extremely high levels of sizing. The biggest technological challenge at the moment in research into AKD sizing is to find a method of application of these dimers which allows high levels of reaction at lower levels of addition. Levels of reaction in ASA sizing are equally important but for another reason, namely that the unreacted material can hydrolyse quickly and desize the sheet.

One of the most important differences between AKD and ASA sizing is that, in the case of the latter, reaction with cellulose and sizing can be obtained without the sheet temperature having to be raised above ambient. This has important implications for the rate of development of sizing. Sheets sized with ASA have developed their sizing immediately after leaving the drier section of the machine. AKD sized paper, on the other hand, tends to develop sizing over a period of time (often weeks) after leaving the drier section. The final level of sizing for AKD sized paper is therefore often difficult to gauge, and this is obviously a commercial disadvantage.

The fundamental difficulty with reactive sizes is that there will always be competition between hydrolysis and reaction with cellulose. Those sizes which are very reactive towards cellulose are also susceptible to hydrolysis and those which are not susceptible to rapid hydrolysis are rather unreactive towards cellulose. This problem can never be completely overcome whilst paper is made in an aqueous environment. However, some improvements in the chemistry can be visualised. A size which was more reactive than AKD, but whose hydrolysis product did not de-size would have obvious advantages.

The relative rates of reaction of the size molecule with cellulose and the competitive hydrolysis reaction with water will have an important impact on sizing effectiveness. Although a limited amount of work has been done in this area, in particular on the kinetics of the processes and of the interactions between furnish components and additives (217), there is still a need for much further investigation.

ANALYSIS OF SIZES

The ability to measure size content of paper, emulsions and recirculatory white water is of vital importance in the effective remedying of sizing problems on commercial machines. Ideally the analytical procedure needs to be fast, sensitive to the low levels of size used, accurate, free from interference from other wet end components and, ideally, suitable for in-mill use. In addition, for AKD and ASA it is often necessary to discriminate between reacted, unreacted and hydrolysed size. No current method fulfils all of these goals particularly well and much more development is needed.

For ASA and AKD in paper, the unreacted and hydrolysed size is usually extracted from the sheet and then the residual 'bound' size is removed by some chemical process such as base hydrolysis and solvent extraction. Extraction procedures are fraught with difficulty, however, and results are very dependent upon the ability of the selected solvent to access adequately the whole of the sheet structure. The analysis of extracted size is then often done by gas chromatography but, in the case of AKD, conversion by hydrolysis to the ketone is usually carried out prior to measurement by gas chromatography. For bound or esterified AKD, digestion with hydrochloric acid or sodium carbonate is necessary to convert the ester or free AKD via the β keto ester to the ketone. A solid phase extraction system has been developed to determine hydrolysed alkyl ketene dimer in alkaline paper mill deposits (218).

Another procedure which has been used for AKD is that of potentiometric titration. The results agree well with the conventional chromatographic methods, and it also has the added advantage of being more rapid and less complicated (219).

Unreacted AKD can be complexed with 4-dimethyl aminopyridine (DMAP) to produce a coloured derivative which absorbs in the ultraviolet and visible regions of the spectrum. The reaction proceeds quantitatively and displays two absorbances which can be used for analysis. The process is highly sensitive and selective to the dimer in its unreacted form (220,221).

For more sophisticated analytical information, ¹H nuclear magnetic resonance can be used. Impurity content, alkyl chain length and hydrolysis data have been determined in this way for AKD sizes. The proton-decoupled ¹³C NMR spectra of the hydrolysis products of two cationic starches, diethylaminoethyl starch and trimethylammonoylhydroxypropyl starch hydrochloride, have also been used to enable the type and amount of cation to be identified and unambiguously assigned. Samples from paper manufacture often require special solvents or hydrolysis to reduce the molecular weight in order to counter signal broadening (222).

The determination of rosin in paper can also be difficult because a proportion of the rosin is strongly bound to the paper matrix after fixing. Pyrolysis gas chromatography combined with on-line methylation using tetramethylammonium hydroxide has found some application to this problem. The products for analysis are the methyl esters of the rosin adducts. The rosins retained in paper samples have been determined within about 1% standard deviation (223).

Special procedures have also been found to be necessary to determine calcium soaps in pitch deposits or aluminium soaps in rosin sizing. Sequential extraction with hot acetone and chloroform alone, cannot quantitatively separate aluminium soaps from wood resin in deposits because the aluminium soaps are only partially soluble in hot acetone and chloroform. Initial extraction of a deposit sample with acetone at room temperature to remove wood resin, and/or hydrocarbon oils, followed by the decomposition of metal soaps by refluxing with acidic acetone yields metal bound acids and aluminium chloride precipitate. Atomic absorption spectroscopy can then be used after dissolution in acidic water to quantify aluminium in the precipitate. Resin acids bound to the metal are extracted and analysed by gas chromatography or gas chromatography-mass spectrometry (224).

The quantitative determination of aluminium species in rosin-alum sizing is relatively simple. It can be done by ashing the sample followed by atomic absorption or x-ray fluorescence. 8-hydroxyquinoline staining of alum has also been used in conjunction with differential interference contract microscopy and scanning electron microscopy to determine the alum distribution in paper (225). Aluminium can also be measured by means of the specific fluoride ion electrode. The method also allows alum content to be continuously monitored and alum feed to be controlled (226).

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Transcription of Discussion

A review of advances in internal sizing

Professor John Roberts, UMIST, UK

Anton Esser, BASF, Germany

You showed this NMR spectra and there were two peaks. I do not understand what it was. Was it a β -keto-ester?

John Roberts

No, it was simply demonstrating that you could see the free AKD in a sheet of paper. Those had not actually been heat treated in anyway. Really you need to heat treat them before you can stimulate any β -keto-ester formation.

Anton Esser

To your knowledge are there any NMR spectra which show a β-keto-ester?

John Roberts

I think the that work in the published papers of the Hercules Group does show some support. I have read the paper which is coming up later this morning and, of course, there is some evidence the other way. Possibly the ester peaks in that paper have been misinterpreted in terms of trapped C^{13} carbon dioxide. Perhaps we can discuss it when the paper comes up. At the moment I think I favour β -keto-ester formation.

Kevin Hodgson, Associate Professor, University of Washington, USA

Thank you for a very informative and comprehensive review. When one looks at the spectrum of polymers available and considers the natural hydrophobicity of so many of these materials and the fact that also they can contain certain reactive functional groups, either naturally or by design, you wonder about their use as sizing materials. Do you have some comments or thoughts about why we don't see more polymeric materials as internal sizes?

John Roberts

Only the ones that come straight from the top of my head, I've not given an awful lot of thought to it. I imagine it could be tied up with the problem of forming emulsions in the first place. There seems no theoretical objection to them. In fact they ought to be fairly good but, perhaps emulsion formation is difficult. There may be representatives of the size supply companies who want to comment on this. Certainly these have been tried at laboratory level but why they haven't come to commercial use I'm really not too sure.

Gil Garnier, Research Engineer, Paprican/McGill, Canada

AKD and ASA are emulsified prior to the addition of the furnish and typically we use a polyelectrolyte and a large quantity of it. My questions are the following. Does the internal size react with the polyelectrolyte and what's going on with the polyelectrolyte in the reaction?

John Roberts

It's been speculated on before and it's a difficult question to answer. If you want my own views, I think it's virtually impossible that you would have any covalent reaction taking place in the emulsion between the size molecule and the stabilising polymer. However, it's fairly clear that, as the sheet dries, the polymer and sizing molecule will be in close proximity. They have reactive functional groups, so that you might reasonably expect some measure of reaction to take place. It may not actually matter too much in terms of sizing efficiency however.

Gil Garnier

But why not because if we take the case of starch it has exactly the same hydroxyl group as cellulose. Why can't it react with AKD?

John Roberts

I think it would.

Gil Garnier

So basically what we would have is two types of sizing. We have AKD reacting with the hydroxyl groups of cellulose and also AKD sizing the starch which starch could then absorb on the furnish.

John Roberts

That's quite possible, yes, and it would be almost impossible to distinguish between those two cases. Certainly C^{13} NMR or FTIR will not easily answer those questions. *Bruce Lyne, Senior Manager, International Paper, USA*

One dimension you didn't bring out in your talk about sizing is that sizing essentially defines the surface chemistry of the paper, which can be important for a number of attributes other than holding out water, such as adhesion. In particular it can be quite important for the adhesion of toners and inks to paper. I think that rosin has been very popular and people are still struggling to use rosin on the alkaline side because it is a very good material for adhesion and slip. This may be due to the fact that its somewhat more complex than you have portrayed. It's actually a rather nasty mixture. The solubility envelope for such a complex material is actually very large and therefore it will give adhesion to a broad range of different toners.?

John Roberts

Yes, I would agree with that. I did mention specifically the question of adhesion in the written review and it is clear that there are very sharp differences in adhesion properties between the different sizing systems. If that is a key property that you are trying to induce then it must be considered along with the sizing properties you are trying to achieve. I also agree that rosin is a much better material in terms of slip and adhesion than AKD or ASA.

Bob Proverb, Group Leader, Cytech Industries, USA (in answer to Kevin Hodgson's question)

Based on some of the work that we have done in our laboratories, one of the reasons why we believe that polymeric sizes are not efficient is because of a lack of mobility on the fibre surface. One of the issues with using molecular sizes such as ASA and AKD is the

mobility of these materials once they are on the surface. As the emulsion comes on to the surface of the fibre, it breaks and then can spread across the fibre surface and cover the molecular area on the surface. Polymeric sizes do not possess the thermodynamic freedom in spreading over the surface as do the individual molecules in the synthetic size emulsion. As a result, this leads to poorer efficiency of these sizes as more material must be used to gain the same hydrophobic coverage on the fibre surface.

Peter de Clerck, Division Manager, Avebe (Far East) Pte, Singapore

You mentioned that there seemed to be a significant correlation between the types of fillers and the problems of sizing reversion and deposits. In the Far East there are a number of new machines going in. They are undergoing the conversion from acid to alkaline papermaking which Europe underwent 10-15 years ago. Looking at the results on those machines, there have been very strong correlations between the fillers used and the problems with the sizing with AKD.

John Roberts

In terms of reversion?

Peter de Clerck

Yes. Particularly with the calcium carbonates used. There is a strong correlation between the amount of calcium carbonate, the surface area of the calcium carbonate and the free alkalinity in the calcium carbonate. Measurements of the bicarbonate alkalinity correspond directly to the incidents of problems of sizing reversion and it's probably by the same mechanism that Prof Lindström proposed in his series of papers in Nordic Pulp and Paper some years ago.

John Roberts

Is that in-house company information or is it published?

Peter de Clerck

No it's not published it's just from a series of observations on a very large number of machines.

John Roberts

It's the kind of information that one hears all over the place and there clearly is a problem with reversion particularly with calcium carbonate systems. I think Tom's work was to do with the catalysis of ester formation rather than reversion. Do you want to comment Tom?

Professor Tom Lindström, Royal Institute of Technology (KTH), Sweden

Yes, we work with ester formation but not reversion but obviously the alkalinity of the calcium hydroxide in the PCC is catalysing the hydrolysis of the ester.

John Roberts

Yes you would expect base catalysis in those systems.

Lars Wågberg, Research Manager, SCA Research, Sweden

In your summary you mentioned that the polyaluminium chloride does not form aggregates but it does. That's a minor comment. Linked to that comment, thinking about the instability we find when we talk about rosin sizing in alkaline pH is this something which you can recommend to papermakers who want a stable wet end?

John Roberts

Yes neutral rosin sizing is widely practiced as routine technology in Europe.

Lars Wågberg

Yes we have it in a couple of our mills but it is not giving an especially stable system so I agree with you that a lot of research has to be done.

John Roberts

It may depend on the type of system, and perhaps our mills in the UK are somewhat different with high levels of recycled fibre. It certainly works well and consistently and has done over a number of years in quite a number of mills in the UK.