PAPER'S RESISTANCE TO WETTING – A REVIEW OF INTERNAL SIZING CHEMICALS AND THEIR EFFECTS

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This review considers research related to internal sizing agents. Such chemicals, when added as emulsions or in micellar form to slurries of cellulosic fibers before paper is made, can make the product resist water and other fluids. Significant progress has been achieved to elucidate the modes of action of alkylketene dimer (AKD), alkenylsuccinic anhydride (ASA), rosin products, and other sizing chemicals. Recent findings generally support a traditional view that efficient hydrophobation requires that the sizing chemicals contain hydrophobic groups, that they are efficiently retained on fiber surfaces during the papermaking process, that they become well distributed on a molecular scale, and that they need to be chemically anchored. A variety of studies have quantified ways in which internal sizing treatments tend to be inefficient, compared to what is theoretically possible. The inefficient nature of chemical and physical processes associated with internal sizing, as well as competing reactions and some interfering or contributing factors, help to explain apparent inconsistencies between the results of some recent studies.

Keywords: Internal sizing, Hydrophobicity, Cellulosic fibers, Paper, Mechanisms, Curing, Liquid penetration, Rosin, ASA, AKD

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INTRODUCTION

The term "internal sizing" is used by paper technologists to describe the practice of adding chemicals to aqueous slurries that contain cellulosic fibers, so that the resulting paper is able to resist water or other fluids (Davison 1975, 1986; Keavney and Kulick 1981; Reynolds 1989; Crouse and Wimer 1990; Eklund and Lindström 1991; Hodgson 1994; Roberts 1997; Neimo 1999; Hubbe 2000, 2005). The process can seem like magic. Very small amounts of additives are able to overcome the inherent wettability of the cellulose and hemicellulose (Hansen and Björkman 1998), two of the main chemical components of ordinary paper. The widespread success of internal sizing can seem even more improbable when one considers the fact that a typical sheet of copy paper has a thickness equivalent to the widths of only about seven layers of cellulosic fibers, and over half of the space within a typical sheet of paper or paperboard is occupied by air (Scott et al. 1995). Various other authors have reviewed ways in which changes in the free energy of surfaces is likely to affect the passage of liquids through the tiny pores that exist within a sheet of paper (Davison 1975; Keavney and Kulick 1981; Eklund and Lindström 1991). To add to the challenge, the chemical additives need to be formulated in such a way that they are compatible with the aqueous mixture, something that would appear to contradict the stated objective of being able to make the paper resist aqueous fluids. Typical

addition levels of the most efficient internal sizing agents lie in the range of 0.05 to 0.25%, based on the dry weight of paper. These tiny amounts of additives explain the wetting characteristics of paper cups and inkjet printing papers, making such products very different from paper towels and blotter paper.

Why Treat the Fiber Slurry to Hydrophobize Paper?

In the broadest sense, paper products can serve three main functions. They can be used for communication, for containing materials, and for absorbing or wiping liquids. Sometimes two of these functions are combined, as in the case of the cereal boxes, which use multi-color graphics to grab your attention. All of these functions can be highly dependent upon the degree to which fluids are able to spread onto or penetrate through the material. What is often overlooked is that internal sizing agents also can have a large effect on the paper manufacturing process itself. The process efficiency can be affected, and sizing can affect the hold-out materials, such as starch solutions, which are applied to the surface of paper.

Ironically, the end-use performance of absorbent paper products often can be improved by treating the fiber mixture so that the final product is somewhat less absorbent. Excessively rapid wetting can cause a paper towel to come apart before its job of wiping and absorbing is complete. Though wet-strength agents (Wågberg and Björklund 1993; Espy 1995) are widely used for many such applications, such chemicals have limited applicability for paper products that are likely to become disposed in septic systems. A well-chosen treatment with a sizing chemical, at the wet-end of the paper machine, can provide a few seconds of delay in wetting.

More obvious motivations to resist fluid penetration into paper or paperboard can be found in the case of products that are designed to act as containers, but even in those cases, the reasons can be subtle. Modern paper-based cartons for milk and juices have plastic laminate layers on each side. These layers perform the main job of resisting fluid penetration. To save costs, however, most milk cartons have unprotected edges of paperboard that remain exposed to the liquid. The paperboard needs to be internally sized to limit the rate of edge-wicking (Avitsland and Wågberg 2005). Internal sizing also is needed in order to deal with liquid that may pass through pinhole defects in the plastic laminate layers. Requirements for internal sizing of paper are more obvious in such cases as paper cups, paper bags that need to be able to contain wet grocery items, and packing boxes that may be exposed to the rain.

Not all printing processes require that the paper or paperboard be able to resist wetting. For instance, the word "xerography," which describes the operation of common photocopy machines (Borch 1986), means "dry writing." However, many users of xerographic printing paper choose to use the same paper in their ink-jet printers. Insufficient internal sizing can result in feathering of the ink-jet fluid, depending on the type of printer and the amounts of liquid transferred to the page (Barker et al. 1994). Holdout of the colorants in inkjet fluid, near to the surface of paper, is desirable in order to achieve the desired density of print images, while minimizing the cost of the ink.

The efficiency of the papermaking process can be highly dependent on the internal sizing of paper in paper machine systems where the web of product has to pass through a puddle or bath of liquid solution, as in cases where a starch film is applied to

the paper surface (Klass 1990). For example, most paper intended for offset or xerographic printing applications passes through a size press, in which the paper surface is exposed to a hot starch solution. Excessive penetration, before the paper has been dried again, can weaken the structure to such an extent that the frequency of web breaks can increase significantly, hurting the economic viability of the operation. Though size-press breaks are a critical issue for many paper machine operations, the issue has become less important in state-of-art paper machine systems that employ film-press technology (Klass 1990). In such operations, a solution of starch or other hydrocolloid is metered as a thin film onto a roll and then the film is transferred to the paper surface.

Finally, internal sizing can influence the structural characteristics of paper. The best example of this involves the effect of internal sizing on the degree of penetration of size-press starch, which is applied to paper's surface (Barker et al. 1994; Aloi et al. 2001). Such starch can act as a binder, increasing paper's modulus of elasticity. By concentrating such effects near to the paper's surface, one can achieve an "I-beam effect," maximizing the starch's contribution to stiffness (Lee et al. 2002; Lipponen et al. 2005). Starch near to paper's surface also can decrease paper's tendency to transfer lint or mineral components during printing operations (Fineman and Hoc 1978), or to fail when contacted by tacky inks during multi-color lithographic printing operations. The sizing performance of hydrophobic copolymers added at the size press also tends to have a synergistic relationship to internal sizing (Barker et al. 1994; Latta 1994).

What Internal Sizing Does *Not* Accomplish

As a general rule, internal sizing agents generally do *not* contribute significantly to any of the following effects:

- Provide any barrier to vapor, except as an indirect consequence of holding out size-press starch or other water-soluble polymers (Aloi et al. 2001)
- Affect the tendency of fibers in paper to change dimensions in response to changes in humidity (Page and Tydeman 1962; Gallay 1973; Lyne et al. 1996)
- Provide any strength to paper that has become completely soaked with water (Wågberg and Björklund 1993; Espy 1995)

With respect to vapor transport, papermakers can rely on other approaches, including the use of laminated films, as mentioned earlier. High levels of refining, yielding highly dense paper, as well as certain size-press treatments can decrease the vapor permeability of paper (Aloi et al. 2001), though not nearly to the same degree as plastic film.

The reason why internal sizing treatments don't tend to have much effect on paper's dimensional stability, especially under challenging conditions of humidity and temperature, will be considered again towards the end of this discussion. Briefly stated, the effect can be attributed to (a) the tendency of internal sizing treatments to affect mainly the outer surfaces of fibers, and (b) the ability of water vapor to diffuse within the interior of cellulosic fibers, causing them to swell (Page and Tydeman 1962; Gallay 1973; Nanri and Uesaka 1993; Chatterjee et al. 1997).

The Technical Challenges of Internal Sizing

Before considering theories related to the action of internal sizing agents, one can list some challenges that any successful internal sizing system will need to address. A

key challenge consists of the high surface area of the materials that constitute paper. There is a relationship between the required amount of sizing agent and the surface area of the solid materials in paper (Davison 1986; Lindström and Söderberg 1986b). Dried cellulosic fibers often have an air-accessible surface area of about 1-2 m^2/g (Haselton 1955). Much higher values have been found for the accessible surface area of the same fibers before they are dried.

Papermakers use fine mineral particles, *i.e.* "fillers," to achieve opacity, smoothness, and brightness goals. Another common goal of filler use is to decrease the net cost per mass of materials in paper. The dry surface area of filler is typically in the range of 4-20 m^2/g (Bown 1996). As has been shown (Marton and Marton 1983; Riebeling et al. 1996; Voutilainen 1996; Petander et al. 1998), the higher surface area per unit mass of fillers, relative to dry fibers, can lead to a higher uptake of papermaking additives, though the uptake is not necessarily directly proportional to surface area. The amount of chemical required to achieve desired levels of sizing tends to increase with increasing surface area per unit mass of filler (Ozment and Colasurdo 1994) and cellulosic material (Yang et al. 1999; Ramamurthy et al. 2000). As will be discussed, high-area calcium carbonate fillers appear to be somewhat incompatible with certain sizing agents (Moyers 1992). To overcome such problems, it is sometimes recommended to cover up the mineral surfaces with other materials before their addition to the paper machine system (Kurrle 1995). Alternatively, the order of addition of chemical additives and fillers to the papermaking process can be adjusted such that other materials cover the mineral surfaces before the sizing agent is introduced (Moyers 1992).

Surface-active materials, some of which originate in the pulpwood, are well known to counter-act the effects of internal sizing agents (Lindström and Söderberg 1986b; Moyers 1992; Proverb 1997; Yang et al. 1999; Zeno et al. 2005). Avitsland et al. (2006) recently quantified the effects of wood extractives relative to the efficiency of alkylketene dimer (AKD) sizing, depending on how the fibers had been bleached. Other researchers have attributed such effects of bleaching practices to differences in retention efficiency of the sizing agents (Laine et al. 2004).

When kraft fibers swell in water, the pore volume within paper can increase by a factor of four, greatly increasing the size of passages through which water can flow (Avitsland and Wågberg 2005). This effect is especially important in the case of chemithermomechanical pulp (CTMP) fibers.

HOW SIZING WORKS: THEORY

A general hypothesis can be proposed to account for the ability of chemical additives to the papermaking furnish to produce resistance to aqueous fluids in the final paper. A subsequent section will then evaluate these ideas relative to findings in the case of four main types of internal sizing agents – alkenylsuccinic anhydride (ASA), alkyl-ketene dimer (AKD), rosin products, and copolymer products.

Many aspects of the hypothesis to be described already have been discussed in previous reviews of the subject (Davison 1975, 1986; Keavney and Kulick 1981; Ehrhardt 1987; Reynolds 1989; Crouse and Wimer 1990; Gess 1991; Eklund and

Lindström 1991; Roberts 1991, 1997; Hodgson 1994; Neimo 1999; Hubbe 2000). It is generally agreed that resistance to the spreading or penetration of water requires a reduction in the free energy of paper's surface (Krueger and Hodgson 1995; Irvine et al. 1999). Aqueous fluids spread and penetrate with relative ease in the case of "bare" cellulosic surfaces, due to the ability of water to form hydrogen bonds with the surface hydroxyl groups of the polysaccharide-rich material. The relatively high energy of interaction results in relatively low contact angles of water with cellulosic materials (where, by convention, the angle of contact is drawn through the liquid phase). By contrast, when a drop of water is placed onto a flat, non-wetting plastic surface, by definition, the angle of contact is greater than 90 degrees. Thus, the internal sizing of paper can be envisioned as a way to transform the paper surface from a relatively high-energy state, rich in groups capable of hydrogen bonding, to a modified state in which the free energy of the surface is reduced.

To account for this transformation, the following general hypothesis can be proposed for the action of an effective internal sizing additive:

1. A hydrophobic entity, such as an alkyl group having about 16 or more carbons, must be included in the active ingredient of the sizing agent.
2. The active ingredient must become well dispersed after its addition to the fiber-containing suspension, for instance as an emulsion or micellar solution.
3. The sizing agent must remain in its active form up to a critical point in the papermaking process.
4. The sizing agent must be retained efficiently in the wet-web of paper.
5. The sizing agent must become molecularly well distributed on the outer surfaces of the paper by the time it is dried.
6. Individual molecules of the sizing agent must become anchored and oriented in order to achieve a stable and efficient sizing effect.

Retain in the Wet Web

To be effective, it is essential that sizing additives become retained on solid surfaces within the paper, as it is being formed. Non-retained sizing materials either may pass out of the system with the excess water sent to the waste treatment system, or they may circulate long enough in the process so that they suffer physical or chemical changes, making them less effective. Unretained sizing agents also may deposit onto wetted surfaces within the paper machine system (Petander et al. 1998). Though some kinds of sizing additives are formulated in such a way that they have a natural attraction for cellulosic materials, it is often satisfactory if the material is capable of being retained by commonly used coagulants and retention aid polymers (Norell et al. 1999).

Distribute on Surfaces

Divergent opinions have been offered regarding how internal sizing agents become distributed over the surfaces of fibers as paper is being made. The broad term "distribute" has been chosen in order to encompass various explanations. In the case of rosin soap sizes there is general agreement that the active ingredient usually becomes chemically precipitated onto surfaces as a consequence of treatment with soluble

aluminum species (Back and Steenberg 1951; Strazdins 1977, 1984; Ehrhardt 1987; Marton 1989). In the case of other sizing agents, such as rosin emulsion products, ASA, and AKD, one traditional explanation is that the active ingredients of size are in liquid form under the conditions prevailing during the drying of paper, allowing them to flow and spread over paper's surface (Dumas 1981; Davison 1986; Fischer 1999; Lindfors et al. 2005). More recently, much attention has been paid to factors affecting the diffusion of monomolecular or multi-layer films adjacent to a liquid droplet of sizing agent (Seppänen and Tiberg 1999; Garnier and Godbout 2000; Shen and Parker 2003; Shen et al. 2003). In addition to these possible mechanisms, there also is good evidence that molecules of certain sizing agents become vaporized under drying conditions, making it possible for them to recondense onto adjacent surfaces (McCarthy and Stratton 1987; Back and Danielsson 1991; Gess 1991; Yu and Garnier 1997; Shen et al. 2001; Gess and Rende 2005). The latter mechanism is sometimes disputed, possibly due to the fact that some sizing agents can decompose to non-sizing species while in a humid vapor (Akpabio and Roberts 1987; Laitinen 1999; Hutton and Shen 2005; Shen et al. 2005). As will be discussed, it appears likely that two or more of these mechanisms contribute to effects that are commonly observed during production of a typical sized paper product.

In addition to the question of "how," it is also important to ask "when" do typical sizing agents, other than rosin soap products, become distributed over the surfaces in a sheet of paper. An important clue is provided by the fact that heat and time are required, and sizing does not develop significantly until after the paper has become dry (Davis et al. 1956; Lindström and Söderberg 1986). It has been suggested that the presence of liquid water blocks the spreading of sizing agent species over paper's surface (Lindström and Söderberg 1986; Eklund and Lindström 1991). A happy consequence of this situation is that sizing tends to develop only on the outer surfaces of paper, not within bonded areas, where the effect would be expected to adversely affect paper strength.

Anchor and Orient

Why is it the case that the most effective sizing agents – rosin, ASA, and AKD – all happen to have some means by which they might become chemically anchored to solid surfaces? Such anchoring ability appears to be essential in order to maintain an efficient barrier to wetting of paper surfaces (Davison 1975; Dumas 1981; Davison 1986). The idea is that there needs to be some kind of ionic or covalent bonding so that the sizing molecules don't simply diffuse away when confronted by an approaching meniscus of aqueous fluid (Davison 1975). Also, it would make sense that the hydrophobic groups on the sizing agent ought to be kept facing outwards from the surface. Paraffin wax is an inefficient sizing agent, despite the low free energy of its surface (Davison 1986). This lack of effectiveness has been attributed to wax's inability to anchor itself to solid surfaces. As will be seen from the later discussions of ASA, AKD, and rosin emulsion sizing technologies, there is a surprising lack of agreement regarding the degree to which, and even the possibility of various chemical reactions between sizing agents and the solid surfaces of paper. Nevertheless, strong evidence still supports the "anchor and orient" concept as an essential step in the action of efficient sizing agents.

HOW SIZING WORKS: PRACTICE

To support the general sizing hypothesis, as described above, this section considers published findings related to four main types of sizing agents, ASA, AKD, rosin products, and copolymer products. As will be seen, each class of sizing agents shows somewhat unique characteristics. Readers are forewarned not to expect complete agreement among the apparent findings of all of these studies. Some disagreements may be attributed to differences in conditions of treatment or analysis. In other cases there appear to be opportunities for researchers to make further progress in evaluating different molecular explanations of the action of sizing agents.

Case 1: ASA

The use of alkenylsuccinic anhydride (ASA) as an internal sizing agent for paper has grown rapidly since its introduction in the early 1960s (Wurzburg and Mazzarella 1963; Gess and Rende 2005). The active ingredient, in its most commonly available form, exists as an oily liquid at room temperature. The chemical is usually formed by reacting maleic anhydride with an isomerized mixture of linear alkenes having chain lengths in the range of about 16 to 22 carbon atoms. ASA has a relatively high chemical reactivity, making it possible to achieve most of the hydrophobizing effect before the size press of a typical paper machine (Wasser 1986; Daud 1993; Gess and Rende 2005). ASA's high reactivity sometimes has been attributed to the ring strain within the cyclic anhydride group (Davis and Hogg 1983). Reactivity also has been found to depend on the proximity of the anhydride group to other unsaturated groups, which may or may not be in conjugated systems (Rossall and Robertson 1975). As illustrated in Fig. 1, it is generally believed that ASA achieves its most efficient and most permanent sizing effect by forming ester bonds with hydroxyl groups on the polysaccharide components of paper during the drying process.
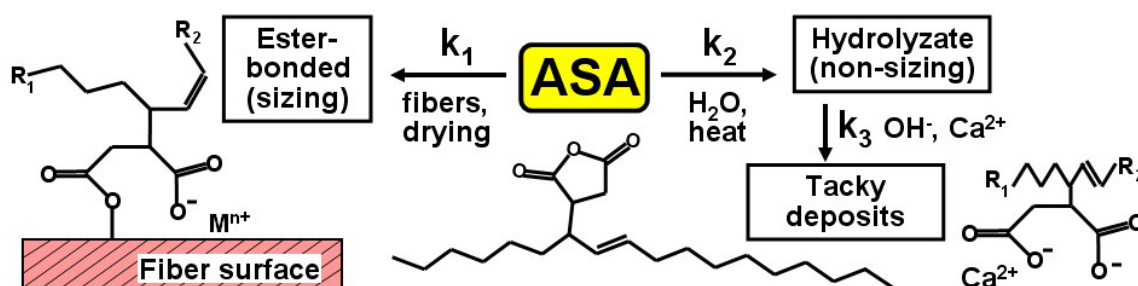

Fig. 1. Summary of main reactions affecting use of alkenylsuccinic anhydride (ASA) size

ASA can be classed as an "alkaline sizing agent," meaning that it can be used effectively in systems containing substantial proportions of calcium carbonate filler. Optimum sizing often is observed at $7.5 < pH < 8.4$ (Savolainen 1996). To be effective under such conditions, the oil needs to be formed into an emulsion before its addition to the paper machine system. Proximity to water during preparation and storage of emulsions, and especially after the material has been added to the paper machine, makes

it impossible to completely avoid an undesired hydrolysis reaction. The hydrolyzed form of ASA, often present as the calcium or magnesium salt of the diacid, cannot be effectively distributed over paper surfaces and tends to form tacky deposits on papermaking equipment. According to Wasser and Brinen (1998), the calcium salt of ASA does not contribute to sizing of paper, whereas the soap form of the ASA hydrolyzate actually tends to reverse the desired sizing effect. Recently it was reported that tackiness could be reduced when ASA was formed from the ethyl esters of mono-unsaturated fatty acids (Isogai and Morimoto 2004).

Cationic starch and related stabilizers

Much effort has gone into optimizing the preparation of emulsions of ASA, usually with cationic starch solutions and controlled hydrodynamic shear (Chen and Woodward 1986; Lee and Shin 1991; Isogai et al. 1996; Proverb 1997; Guan 2002). The cationic starch not only keeps the dispersed droplets from colliding and coalescing; it also helps attach the droplets to the surfaces of cellulosic fibers, fines, and other negatively charged surfaces in the papermaking suspension (Isogai et al. 1996). The word heterocoagulation has been used to describe the retention of positively charged particles of sizing chemicals onto negatively charged surfaces (Lindström and Söderberg 1986b; Robert 1991). Best performance requires that the emulsion droplets be controlled to an optimum diameter, usually near 1 μm (Chen and Woodward 1986). Because excessive hydrodynamic shear can reduce the molecular mass of cationic starch, it is sometimes recommended to initially emulsify the ASA with a minimum amount of cationic starch solution, and then, after the high shear zone, add enough starch to achieve a ratio of about 3-5 parts of starch per part of ASA.

Different types of cationic starch have been found to give very different perform-ance of the sizing agent, when using a specific set of equipment and procedures (Guan 2002). Cationic potato starches were used almost exclusively during the early alkaline conversions of paper machines in the 1980s, but more recently a variety of corn starches, including waxy maize, also have been employed as sources of cationic starch for ASA emulsification. Lee and Shin (1991) found that higher-charged cationic starch tended to achieve higher efficiency of ASA emulsions, when they were used immediately, but the higher-charged starches also tended to speed up the hydrolytic decomposition of dispersed ASA. Lee et al. (2004) observed that a hydrophobically modified cationic starch outperformed ordinary cationic starch, in terms of ASA sizing efficiency. The increased sizing effectiveness was attributed to a smaller droplet size.

Not all paper mills have starch cooking equipment. In addition to pregelatinized cationic starches, which do not require cooking, various synthetic polyelectrolytes have been used for ASA emulsification. Rendé and Breslin (1987) patented the use of various cationic copolymers, including acrylamide products, for use as ASA stabilizers. Shigeto and Umekawa (1992) claimed the use of amphoteric acrylamide for similar applications, and reported good storage stability and sizing performance of the emulsions.

Hydrolysis and its consequences

One reason why the size of droplets plays such an important role in the optimiza-tion of ASA systems is that smaller droplets have higher surface area, making the

anhydride more susceptible to the undesired reaction with water, before the material can be retained in the paper web and cured in the dryer section of the paper machine. Wasser (1987) showed that the rate of ASA hydrolysis during storage of emulsions tended to increase with increasing pH and temperature. An observed acceleration with time of the hydrolysis reaction (Wasser 1987) suggests that the decomposition products accelerate the reaction. This makes sense, since carboxylate species would be expected to increase the concentration of water that diffuses within a droplet of ASA.

To slow down the rate of hydrolysis, some papermakers employ strategies in which the starch solution, to be used for ASA emulsification, is buffered into the acidic range by addition of such substances as adipic or citric acid or aluminum sulfate (papermakers' alum). Scalfarotto (1985) found that the presence of aluminum species in the process water also tends to reduce the tackiness of any ASA hydrolyzate that happens to form. Thus it was possible to overcome picking problems at the wet press by alum addition to the paper machine. At the same time, the aluminum salts also tended to boost the sizing efficiency of ASA (Scalfarotto 1985; Zandersons et al. 1993; Lee and Shin 1991).

Vapor Distillation

McCarthy and Stratton (1987) reported that ASA can volatilize during the drying of paper. Papermakers using ASA often find evidence of vapor-phase transport of the sizing agent. ASA byproducts can be found on the hoods of paper machines, either in isolation, or mixed with other materials (Gess and Rende 2005). The amounts of such deposits could be reduced by increasing the molecular mass of the ASA, *i.e.* by increasing the lengths of the alkenyl groups. Back and Danielson (1991) showed that ASA sprayed onto one side of a paperboard sheet was able to migrate and develop hydrophobicity throughout the thickness of the product. The ability to size the opposite side of the sheet increased with increasing temperature and time.

Ester bond evidence

Though various methods are available for detection of ester bonds, such as those most likely to form between ASA molecules and the hydroxyl groups of cellulose, hemicellulose, and starch molecules on fiber surfaces, it has been very challenging to quantify such reactions. One faces the problem of trying to observe a relatively small quantity of bonds formed at an interface. Meanwhile, the most commonly used analysis methods, such as infrared (IR) absorption spectroscopy, also detect signals that result from the adjacent bulk phase or phases (Dumas and Evans 1986). The problem of sensitivity is compounded by the fact that relatively little ASA is needed in order to size paper, *e.g.* of the order of magnitude 0.1% addition on a solids basis. Even to quantify the amount of ASA that is retained in paper, it is necessary to use methods that are ultrasensitive to surface-bound features, *i.e.* surfaced-ionization mass spectrometry (SIMS) (Brinen and Kulick 1996). McCarthy and Stratton (1987) carried out reactions in dimethylsulfoxide (DMSO), using Fourier-transform infrared (FTIR) spectroscopy to show that ASA is capable of forming ester bonds with cellulosic hydroxyl groups. Subsequently they and others showed that ester bonds also can form under realistic conditions of ASA sizing (McCarthy and Stratton 1987; Zandersons et al. 1993).

Isogai and coworkers, using a variety of experimental approaches, found little or no evidence of ester bond formation during ASA sizing. Though some of their results probably can be attributed to the sensitivity issues mentioned earlier, much of the added ASA was converted to the hydrolysis product during sizing, and only a small proportion, if any, formed an ester bond with the fiber (Nishiyama et al. 1996a; Isogai and Onabe 1996). Most of the ASA products could be removed from sized sheets by a hot aqueous micellar solution of nonionic surfactant, an observation that would not be expected in the case of ester bonds to a surface (Isogai 1998). To explain why unreacted ASA was required in order to achieve sizing, it was proposed that only the anhydride form can be efficiently distributed onto fiber surfaces (Isogai and Onabe 1996; Nishiyama et al. 1996b; Isogai 1998). Another explanation is that the authors sometimes may have employed conditions in which the ASA had a greater opportunity to react with water, relative to typical conditions in the dryer section of a paper machine, *i.e.* relatively large ASA dosages and relatively slow rates of drying.

Theories proposing that ASA achieves sizing by means of the diacid form of the chemical may receive some measure of credibility by reference to work carried out under acidic conditions. Hatanaka et al. (1991) showed that it is possible to employ the diacid soap of ASA in very much the same manner that one would size with rosin soap products (see later). The pH needed to be below 5.5 and at least 1% alum addition produced the most effective sizing, even exceeding the effect of a fortified rosin soap product. One might expect such a reaction to be possible, even under alkaline papermaking conditions, if the surfaces have sufficient coverage by aluminum or calcium species, capable of forming the stable, insoluble salts with the additive. Novak and Rendé (1993) suggested, however, that ASA molecules adsorbed onto calcium carbonate surfaces can more easily revert to a non-sizing form during storage of the paper. In summary, though there is good evidence that ASA forms ester bonds at the paper surface during drying, there is also evidence that much of the ASA can end up in an unbonded or weakly bonded state.

Assuming, for the moment, that ASA's contribution to sizing is mainly due to ester formation, it still remains unclear whether or not much of the esterification takes place between ASA and starch products, rather than with cellulose or hemicellulose. No study addressing this point was located while searching the literature for this review. Factors suggesting a significant role for ASA-starch reactions include (a) the proximity of ASA and starch, following preparation of starch-based emulsions, (b) the flexibility and non-crystalline nature of starch chains, which would be expected to make the hydroxyl groups available for reaction, and (c) the fact that ASA sizing efficiency often increases with increasing ratios of cationic starch that is added concurrently with the ASA.

Molecular architecture effects: Sweeping and protection

At the start of this discussion of ASA characteristics it was mentioned that the alkenes from which ASA is synthesized typically are isomerized. This is done to obtain a mixture of products having their double bonds usually located towards the central part of the molecule. From a practical standpoint, the transformation reduces the melting point of ASA, so that ASA emulsions can be prepared at relatively low temperatures. In addition, the isomerized form of ASA tends to out-perform ASA that has been prepared from primary alkenes (Roberts et al. 1993; Smith 1999). The higher performance of the

commonly used isomerized form of ASA was attributed to the shape of the molecule, roughly resembling a "T," bound to the fiber at its base. The alkyl group, situated above the anchoring group of the ASA, can be expected to protect the ester bond, as well as the carboxyl group that becomes left over during the proposed ester-forming reaction with the fiber surface (see Fig. 1). The alkyl group also may be able to sweep itself around, preventing the advance of a front of aqueous solution over that part of the fiber.

Case 2: AKD

Alkylketene dimer (AKD) products, which usually are prepared by dimerization of stearoyl chloride (Hodgson 1994), provide a second set of examples that can be used when attempting to define the essential characteristics and actions of efficient sizing agents. Already at the time of its introduction, the inventors of AKD sizing technology were convinced that a chemical reaction takes placed between the active ingredient and hydroxyl groups at the fiber surface (Davis et al. 1956). Similarly to the ASA products just discussed, AKD needs to be emulsified in the presence of cationic starch or other cationic polymers, before it can be added to paper machine systems. But AKD is so much less reactive than ASA that the emulsification can be carried out at a central facility, allowing shipment of ready-to-use AKD dispersions to paper mills. Like ASA, AKD tends to perform best at neutral to weakly alkaline pH, making the product suitable for making paper that contains calcium carbonate filler. Due to AKD's relatively low reactivity, papermakers often over-dry paper before the size press to cure the size. In many cases, full sizing is achieved only after the reels and rolls of paper have gradually cooled for several hours or days (Kamutzki and Krause 1983; Roberts and Garner 1985).

Some differences in performance of AKD and ASA sizing agents can be traced to differences in the physical state of the active ingredient. Neat AKD is a waxy solid at room temperature. Not surprisingly, over-use of AKD can result in slippery paper (Hoyland and Neill 2001; Karademir and Hoyland 2003), though some researchers blame a breakdown product of AKD, rather than AKD itself for observed decreases in the coefficient of friction (Karademir et al. 2004). As delivered to the paper mill it is expected that AKD dispersion can contain the ketone byproduct of hydrolysis (Asakura et al. 2006b), as well as oligomers of alkylketenes (Asakura et al. 2006a) and fatty acids (Asakura et al. 2005). Most sources agree that such impurities decrease the overall effectiveness of AKD products (Isogai et al 1992; Asakura et al. 2006ab) and make it more difficult to prepare stable dispersions of AKD (Asakura et al. 2005). One study found, on the contrary, that sizing efficiency improved as the content of hydrolyzed products increased to about 25% (Isogai et al. 1994). Impurities, as well as the chain lengths of the alkyl groups within AKD can affect the melting point of the material, a factor that has been found to correlate well with certain deposit problems if the melting point is close to the temperature of the process water (Knubb and Zetter 2002). AKD having a somewhat higher molecular mass, *i.e.* having longer alkyl groups, has been found to form dispersions with higher stability, presumably due to the less tacky nature of the active ingredient (Chew et al. 2004).

The theory that slipperiness problems with AKD-sized paper are due to AKD itself, rather than due to byproducts, finds support in observations that the problems can be substantially overcome if there are unsaturated groups within the hydrocarbon tails of

the reagent. Alkenylketene dimer (AnKD) products have been used effectively for the sizing of paper products intended for precision sheet-fed printing, an application that can be highly sensitive to slippage (Brungardt and Gast 1996; Kenton 1996).

Figure 2 summarizes commonly held concepts of how AKD molecules become distributed and bound to cellulosic fiber surfaces. Issues related to distribution pathways and relative rates of reaction will be discussed later. It is widely believed that the fraction of AKD molecules that are able to form β-keto ester bonds with hydroxyl groups at the surfaces of papermaking materials play a central role in achieving the observed increases in resistance to aqueous fluids (Davis et al. 1956; Karademir et al. 2004). By contrast, efforts to make paper hydrophobic by treating it with the ketone byproduct of AKD usually fail (Karademir et al. 2004), and unreacted AKD does not appear to contribute significantly to the sizing effect (Karademir and Hoyland 2003).
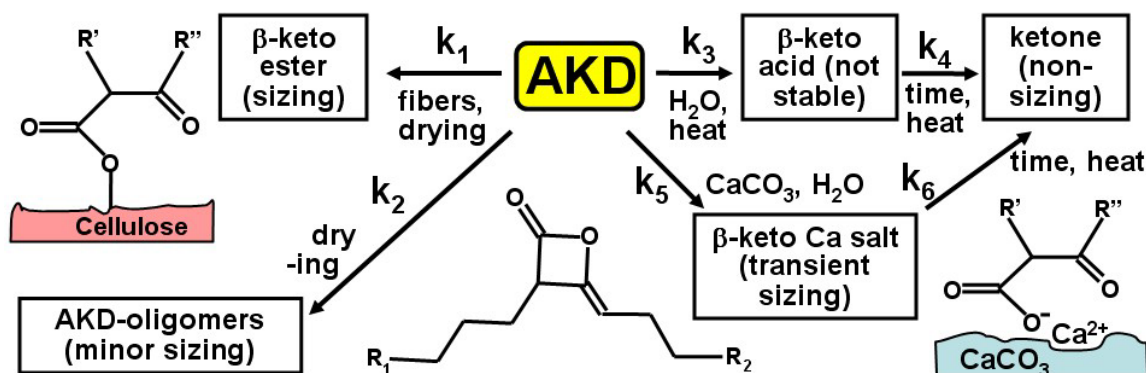

Fig. 2. Summary of main reactions affecting alkylketene dimer (AKD) sizing agents

Emulsification at the supplier plant

Dispersions of AKD particles are often called "emulsions," due to the fact that the active ingredient is melted just before the process of dispersion. The term "dispersions" will be used here, in recognition of the fact that AKD exists as solid particles in the formulations that are received by papermakers. The most commonly used stabilizers for AKD include cationic starch products (Knubb and Zetter 2002; Chew et al. 2004), cationic amido-amine epichlorohydrin products, which are well known as wet-strength agents (Espy 1995), and other cationic synthetic polyelectrolytes (Esser and Ettl 1997). The function of the stabilizers is to prevent particles of AKD from colliding and sticking together. The effectiveness of starch products in maintaining stable dispersions has been found to increase with increasing molecular mass (Chew et al. 2004). A severe way to evaluate the effectiveness of different stabilizing systems involves subjecting AKD emulsions to thermal shock cycles; such tests have shown that the presence of fatty acids (Asakura et al. 2005) and stearic anhydride (Asakura et al. 2006b) tend to make AKD dispersions less stable. Asakura et al. (2006b) found evidence that the presence of impurities in AKD wax tended to accelerate further hydrolysis, an effect that mirrors some findings in the case of ASA (Wasser 1987).

Even with a good stabilizing system and use of refrigeration, excessively long storage of AKD emulsions can be expected to result in significant hydrolysis, reducing

the efficiency of sizing (Isogai et al. 1992). Esser and Ettl (1997) found that the rate of hydrolysis of AKD tended to be faster in the case of dispersions stabilized by polyethyleneimine (PEI), in comparison to cationic starch as a stabilizer.

Retention of AKD during paper forming

Because AKD usually is added to paper machine systems having neutral to alkaline pH, conditions under which hydrolysis is accelerated, it is important that the product be retained efficiently (Davison 1986; Cooper et al. 1995; Esser and Ettl 1997). Material that is not retained during the first pass through the forming section will tend to break down, to some degree, as it remains an unnecessarily long time in contact with the alkaline process water.

Electrostatic factors appear to play important roles in AKD retention (Lindström and Söderberg 1986b, Isogai 1997; 2004a; Ravnjak 2006). Thus, negatively charged colloidal materials in the paper machine process water are expected to neutralize the cationically stabilized AKD particles, interfering with their adsorption onto cellulosic solids. The importance of negatively charged groups on fiber surfaces in retention of AKD particles stabilized by cationic polyelectrolytes was demonstrated by selectively blocking carboxylate groups (Isogai et al. 1997); less of the AKD was retained on aminated pulp. Similarly, Johansson and Lindström (2004a) found increasing retention efficiency of AKD onto fibers having increasing negative charge density. Though specific cationic polymers have been found to promote retention of AKD products (Moyers 1992; Hasegawa et al. 1997; Isogai 1997), it is usually sufficient just to aim for relatively high overall retention of fines, using conventional retention aid products (Johansson and Lindström 2004ab). As shown by Marton (1991), the amount of AKD that becomes attached to fiber fines and fillers tends to be out of proportion to the mass of those solids. Riebeling et al. (1996) observed that sequential treatment of the furnish with a hydrophobically modified amphoteric polymer was able to direct more of the AKD onto cellulosic surfaces, rather than the surfaces of calcium carbonate.

Composition and migration of AKD vapors

Though there is good reason to expect that vapor migration plays some role in AKD sizing, various studies have suggested that much of the material may be converted to the non-sizing ketone form, perhaps as a consequence of being present in a humid vapor phase. Akpabio and Roberts (1987) concluded that there was sufficient water even in "dry" paper to be able to convert palmitic AKD to palmitone. The vapor-phase treatment did not result in a significant hydrophobic effect, even though byproducts of AKD could be detected in the treated paper. Likewise, Hutton and Shen (2005) saw no development of sizing when AKD-saturated paper was separated from untreated paper by an air gap and heated to 105 ^{o}C or 175 ^{o}C. Results were consistent with the transfer of ketone, rather than active AKD. Laitinen (1999) observed considerable migration of ketone byproducts of AKD to an untreated sheet of wet paper applied to the wet web of AKD-treated paper on a pilot paper machine. Shen et al. (2005) observed that the vapor above heated AKD consisted mainly of fatty acids, rather than AKD or its ketone byproduct. It appears that similar chemical phenomena may underlie the ineffectiveness of AKD as a sizing agent under conditions of impulse drying, especially in the case of

relatively long pressing times (Mendes et al. 2003ab).   Rather than proving that AKD does not migrate in vapor, as part of the sizing mechanism, the observations cited above suggest that effective AKD sizing requires a relatively narrow range of conditions. Such conditions might be achieved more easily in a real paper machine system, in contrast to artificial curing conditions that have been used in certain mechanistic studies.

Evidence favoring vapor deposition, as a mechanism of distributing AKD to sites on the paper surface where it can contribute to sizing, was provided by Davis et al. (1956). Sizing was achieved throughout paper's thickness when it was applied just to one side. Yu and Garner (1997) demonstrated vapor-phase sizing by AKD in sealed tubes. Increased bicarbonate alkalinity and polyethyleneimine (PEI) treatment of the paper, during its initial preparation, tended to increase the rate at which water contact angles increased, due to the vapor-phase sizing. Shen et al. (2001ab) observed sizing on uncovered surfaces that were heated adjacent to AKD-sized paper sheets.

Vapor distribution appears to play a further role in the development of AKD sizing effects after a size press. Brungardt (1997) reported cases in which over-drying of AKD-sized paper before a size press resulted in *less* sizing effects after starch had been applied and the paper had been redried. The effects were attributed to the ability of unreacted AKD in the paper to diffuse through the sheet and react with the starch layer on the paper in the after-size-press dryers. At high levels of AKD treatment there was no advantage of under-drying the paper before the size press, since there was always plenty of unreacted AKD in the paper, ready to take part in the proposed vapor-phase effect.

Before leaving the subject of vaporization, some comment should be made regarding molecular mass. If one were to form both ASA and AKD from 18-carbon alkanes and alkenes, the molecular mass of each AKD molecule would be about 1.5 times that of each ASA molecule. Each AKD molecule, being a dimer, contains two of the alkyl chains, whereas the ASA contains only one. All things being equal, higher molecular mass implies a lower partial pressure as a function of temperature. On that somewhat discouraging note, with respect to vapor-phase sizing with AKD, it makes sense to inquire about other possible mechanisms. Likewise, according to Dumas (1981) the relatively low volatility of stearic anhydride has been one of the primary reasons why it failed to achieve widespread use, in competition with ASA and AKD.

Spreading evidence

Considerable progress has been achieved recently with respect to evaluating the extent to which AKD is capable of spreading on heated cellulosic surfaces, either by bulk-phase flow or as a thin film. Though the results of bulk-phase surface tension measurements might suggest complete wetting of cellulosic surfaces by molten AKD, results of spreading experiments on smooth surfaces suggest otherwise (Seppänen and Tiberg 1999; Garnier and Yu 1999). For instance, Garnier and Yu (1999) observed isolated patches of AKD on a sized surface by means of atomic force microcopy (AFM). Researchers have observed finite angles of contact between droplets of AKD and various model surfaces representing the fiber (Garnier et al. 1999; Garnier and Godbout 2000).

Given the limited spreading tendency of liquefied AKD onto dry cellulosic surfaces, as just mentioned, researchers have suggested that AKD mainly moves in the form of thin "precursor" films adjacent to the bulk liquid (Seppänen and Tiberg 1999;

Garnier and Godbout 2000). Such spreading may involve multi-layer, in addition to monolayer flow (Shen et al. 2003). In theory, such films may have a lower surface energy than AKD itself, thus impeding spreading of the liquid phase. The advance of molecular films over higher-energy surfaces has been shown to be sensitive to surface imperfections. General roughness, including features perpendicular to the direction of migration, can be expected to halt, or at least slow the progress of a precursor film. In principle, tiny, deep grooves parallel to the direction of migration are expected to promote spontaneous spreading (Garnier and Godbout 2000). However, the cited authors did not expect such a mechanism to be rapid enough, under realistic conditions of paper manufacture, to have a significant effect.

In principle, the spreading within a very thin film would be expected to depend on the effective melting point of the material, the value of which might differ from the bulk melting point. Shen and Parker (2003) detected evidence to support this theory, showing that the freezing point of AKD in a thin film was lower than its bulk value. However, the ketone byproduct of AKD hydrolysis has a higher melting point than AKD itself, and the presence of the ketone appears to impede spreading of AKD precursor films (Shen et al. 2002). Though the ketone has a low surface energy, it apparently does not orient itself in a way such as to be able to achieve effective sizing (Shen et al. 2003). Similarly, the fatty acid component of wood resins can impede AKD sizing, possibly due to their adverse effect on spreading of AKD films (Lindström and Söderberg 1986b; Eklund and Lindström 1991).

To help explain the apparent disagreement among various findings, it has been found that areas of cellulosic surface covered by AKD products tend to be non-uniform, based on dynamic contact angle tests (Shen et al. 2001). Results suggested that much of the AKD-related material became deposited onto fibers as islands, overlying a mono-molecular film at the cellulosic surface. Such an explanation can explain why contact angle tests showed a uniformly hydrophobic surface only after solvent extraction to remove unbound materials (Shen et al. 2001). Taniguchi et al. (1993) found that AKD sizing often improved after treatment of the paper with either solvent or water, followed by redrying. In principle, such procedures can lead to a better distribution of sizing materials.

Covalent reactions

As was made apparent already in Fig. 2, there are various ways in which AKD may potentially react covalently in the course of paper production. Table 1 lists various species that have been detected after the AKD sizing of paper or model substrates, along with literature references tending to support the existence of various species.

The first three AKD-related chemical species listed in Table 1 appear to contribute to the hydrophobation of paper. Support for the formation of covalently bound AKD, the first item in the table, includes the fact that the paper's resistance to water usually cannot be removed by solvent extraction (Davis et al. 1956; Roberts and Garner 1981; Karademir et al. 2004; Avitsland et al. 2006). Ödberg et al. (1987) showed that bound AKD could be removed only when the solvent conditions favored hydrolysis of ester bonds. Bottorff (1993) observed ester peaks in solid-state ^{13}C NMR spectra after extraction of sized paper with tetrahydrofuran (THF).

Table 1. AKD-related Chemical Species Observed after Treatments of Paper or Model Substrates	
Chemical Species	**Literature Citations**
β-keto esters of AKD bound the substrate	Davis et al. 1956; Roberts and Garner 1981, 1985; Lindström and O'Brian 1986; Lindström and Söderberg 1986a; Dumas and Evans 1986; Nahm 1986; Ödberg et al. 1987; Marton 1991; Bottorff 1993; Bottorff and Sullivan 1993; Marton 1995; Chen and Biermann 1995; Karademir and Hoyland 2003; Lee and Luner 2005; Avitsland et al. 2006
Oligomeric species	Roberts and Garner 1985; Bottorff 1993; Hardell and Woodbury 2002
Unreacted AKD	Bottorff 1993; Bottorff and Sullivan 1993; Jaycock and Roberts 1994; Karademir et al. 2004; Lee and Luner 2005
β-keto acids or salts	Rohringer et al. 1985; Bottorff 1993 (minor)
Ketone (hydrolysis product)	Akpabio and Roberts 1987; Bottorff 1993; Marton 1995; Karademir et al. 2004; Seo and Cho 2005

Various authors, using extraction and spectroscopic methods, estimated the proportion of AKD added to paper that eventually forms covalent bonds at fiber surfaces. The fraction of bound AKD was estimated as 34-78% (Dumas and Evans 1986), or up to 60-85% under the most favorable conditions (Lindström and O'Brian 1986). Slow drying conditions seem to favor AKD hydrolysis reactions over esterification (Mendes et al. 2003ab). This can explain why drying temperatures of 120 ^{o}C and above were required to achieve efficient AKD sizing under conditions employed by Kamutzki and Krause (1983). The presence of water appears to impede the distribution of the sizing agent during the early phases of drying (Lindström and Söderberg 1986a), allowing hydrolysis to take place while the sizing reaction is not yet enabled. Under more favorable conditions of drying the activation energy for ester bond formation has been found to be lower than that of the hydrolysis reaction (Lindström and O'Brian 1986), though the difference was found to narrow with increasing temperature (Marton 1995). Seo and Cho (2005) observed mainly formation of the ketone when AKD was reacted with cotton linter cellulose in an ionic liquid solvent system. However, such conditions do not provide any mechanism by which the AKD can be shielded from hydrolysis during a period in which water remains a dominant species in the mixture.

Estimates of the minimum theoretical amounts of sizing agent able to make paper hydrophobic can be obtained from certain studies in which the paper was extracted after treatment with AKD. In theory, solvent extraction is able to remove unbound materials, including unreacted AKD and the ketone hydrolysis product. Though it is less clear whether solvents are able to remove oligomerized AKD or the calcium salts of β-keto acids (see Fig. 2), one usually makes the assumption that the residual concentrations of the latter materials can be neglected. On this basis, Roberts and Garner (1985) found that 0.006 to 0.010% of AKD products, by mass, remained after extraction of sized paper. Dumas and Evans (1986) concluded that between 0.01 and 0.07% coverage of the paper surface by bound AKD molecules was sufficient to achieve sizing. Lindström and Söderberg (1986) reported that between 0.008 and 0.038% of bound AKD, on a mass basis, was sufficient. The lower end of this range was estimated to correspond to just 4% of a monolayer of coverage. The ability of the sizing agent to be effective at such low levels was attributed to rotation and "sweeping" of bound AKD molecules, affecting an

area considerably larger than is occupied by the molecule at any one moment. Marton (1991) estimated that just 20-38% of added AKD ended up becoming chemically bound to the paper surface under practical conditions of manufacture. Cooper et al. (1995) estimated that between 17 and 27% of the added AKD reacted with the paper surface.

Several researchers did not succeed in detecting covalent bonds between AKD and paper surfaces, and they concluded that such bonds may not play an essential role in paper sizing. Isogai (1999), using solid-state NMR, did not detect ester bonds after handsheets formed with AKD addition were dried at 20% or 50% relative humidity, or alternatively in an oven at 105 °C. Follow-up work (Isogai 2000) showed that if β-ketoester bonds had been able to form, they would have been stable to the conditions of enzymatic treatment that were used in the analysis. Likewise Rohringer et al. (1985) failed to detect ester absorbances in IR spectra. Drying was delayed by placing the test samples between pieces of blotter paper. A possible explanation for the results is that the hydrolysis reaction was favored by relatively low temperatures and long exposure times.

In related work, Lee and Luner (2005) observed that non-bound species, such as unreacted AKD, were able to contribute significantly to sizing when there was at least some bound AKD present. The unbound material made its greatest relative contribution to sizing when the bound material was about 0.025% on a mass basis. The synergistic effect, involving bound and unbound molecules to achieve sizing, suggests that the hydrophobic molecules associate with each other at the paper surface. Nahm (1986) observed a related effect in which bound AKD molecules tended to be clustered together on surfaces, suggesting that association between the hydrophobic groups helps to direct unreacted AKD molecules towards hydroxyl groups at the paper surface.

Lee and Luner (2005) also observed that AKD's reaction tended to be more efficient in the presence of humidity, compared to completely dry conditions. Their observations suggest that the presence of moisture increases the availability of surface hydroxyl groups to react with the AKD molecules. In principle, hydrogen bonds that are engaged in intra-molecular or intra-fiber hydrogen bonding would not be available the react with AKD. It would make sense that water molecules, in a humid environment, can displace some of these cellulose-to-cellulose hydrogen bonds, forming structures more accessible to AKD. Similar considerations also can help to explain the greater ease of sizing of never-dried fibers, in comparison to fibers that have been dried one or more times (Davis et al. 1956). Drying results in formation of an increased proportion of intra-fiber hydrogen bonds, and the process is not completely reversible (Stone and Scallan 1966; Hubbe et al. 2003).

Because the hydroxyl groups on paper's surfaces are assumed to play a major role in the formation of any ester bonds with sizing agents, one would expect coverage of those groups with other materials to make paper more difficult to size. Accordingly, Avitsland et al. (2006) observed that wood extractives tended to reduce the amount of AKD that was able to react with bleached kraft pulps.

Oligomers formed during the heating of AKD have been found to contribute to hydrophobicity (Bottorff and Sullivan 1993). However, the effectiveness of AKD oligomers is sufficiently low that their presence in AKD wax was found to have a net negative effect on sizing, in comparison with relatively pure AKD (Asakura et al. 2006).

Cure promoters

If one starts with the assumption that AKD needs to form ester bonds in order to size paper efficiently, as demonstrated by various studies cited above, then if follows that paper technologist are likely to seek ways to encourage such reactions. Investigators have shown that polymeric amines can promote AKD curing (Lindström and Söderberg 1986; Thorn et al. 1993; Kondo and Makino 1993; Cooper et al. 1995; Marton 1995; Mendes et al. 2003c). The fact that the most effective cure promoters of this type contain secondary or other non-quaternary amine groups (Thorn et al. 1993; Kondo and Makino 1993; Cooper et al. 1995), suggests that AKD reacts with such groups during the drying of paper. Some of these studies showed that the same cationic polymers that tended to promote the reaction of AKD in paper sizing also tended to hasten hydrolytic decomposition of AKD after its formulation (Colasurdo and Thorn 1992; Marton 1995). After curing, it has been found that the sizing effects resulting from "promoted" AKD tend to be stable over time, not suffering the "reversion" problems, which will be discussed next (Bottorff 1993). Cooper et al. (1995) suggested, however, that some of the apparent "promoting" effect of amine-type polymers may be due to increased or more uniform retention of the AKD during paper formation.

Increasing bicarbonate alkalinity also promotes the sizing reaction of AKD (Lindström and Söderberg 1986c; Jiang and Deng 2000). Results have been attributed either to a pH buffering effect (Jiang and Deng 2000) or to a lower-energy transition state in the reaction, involving the bicarbonate ion (Lindström and Söderberg 1986).

Sizing reversion

Though only a few authors have offered evidence for the presence of β-keto acids and the corresponding salt forms in paper (Rohringer et al. 1985; Bottorff 1993), it is logical to expect such bonds to form initially when AKD first encounters calcium carbo-nate surfaces when paper is dried. Bottorff (1993) observed transient calcium salts of β-keto acids in freshly-sized paper, but the material reverted to a keto form during storage. This concept can help to explain why AKD-sized papers made with calcium carbonate filler often show significant loss of sizing effects in the days and weeks after the paper is made (Patton 1991; Colasurdo and Thorn 1992; Novak 1993; Bartz et al. 1994; Esser and Ettl 1997). The effect has been found to be more pronounced in the case of precipitated calcium carbonate (PCC) filler (Colasurdo and Thorn 1992; Bartz et al. 1994; Esser and Ettl 1997), an observation that is consistent with the higher surface area of many PCC products, compared to typical ground $CaCO_3$ fillers. Bartz et al. (1994) observed increasingly severe sizing reversion with decreasing particle size and increasing surface area of PCC. Transient salts of β-keto acids can help to explain why the size can be extracted from calcium carbonate surfaces (Voutilainen 1996). Sizing reversion problems often can be reduced by increasing the distance between addition points for AKD and $CaCO_3$, allowing cationic starch or other species to adsorb onto the mineral surfaces ahead of the sizing agent (Esser and Ettl 1997).

Isogai and Asakura (1999) explored other aspects of size reversion, showing that the unsaturated form of AKD tends to be more susceptible to sizing loss when exposed to air-blowing and UV light. Such treatments might be expected to attack the double bonds

within ester-bonded alkenylketene dimer molecules at the paper surface, especially if the electric motor used to blow the air is a significant source of ozone.

Case 3: Rosin Sizes

Rosin-type sizing agents are often called "acidic sizes." They tend to be most efficient in pH ranges of about 4 to 6, depending on the type of rosin and various other factors. Rosin products usually require higher levels of addition, compared to the ASA and AKD sizing agents just discussed. Most rosin is sold either as a dispersion (or "emulsion") of rosin acid particles or as a micellar soap solution. The formulation of dispersion-type rosin products (Ehrhardt and Gast 1988; Shen et al. 2004) is not unlike that of ASA or AKD, except that there is no need to be concerned about hydrolysis. Both forms of rosin product require use of a mordant, such as alum, to fix the hydrophobic molecules to the paper surface (Strazdins 1977, 1984; Marton 1989). In the case of dispersion-type products, interaction with alum mainly takes place during the drying of paper (Ehrhardt and Gast 1988). By contrast, soap rosin products already become precipitated onto fiber surfaces by addition of alum at the wet end of the paper machine (Back and Steenberg 1951). These differences are illustrated in Fig. 3, which uses a fortified rosin molecule for purposes of illustration (see later).
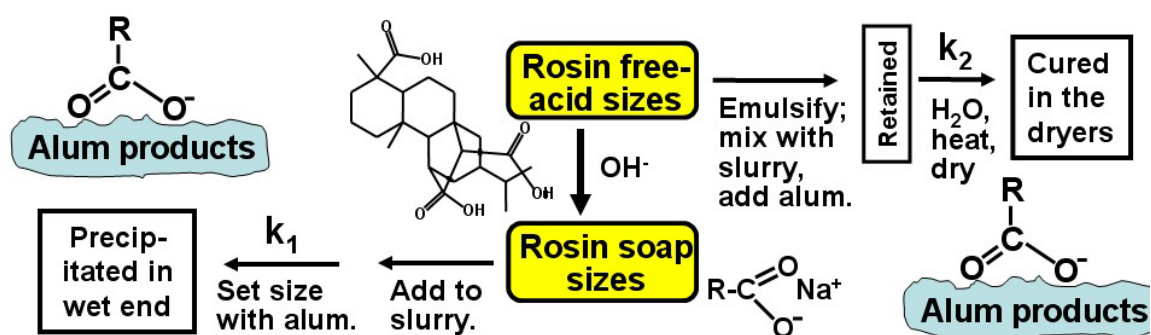

Fig. 3. Summary of the main sizing pathways for two types of rosin sizing agents

The active ingredient of rosin products usually is obtained as a byproduct of kraft pulping. The tall oil that separates from the aqueous phase after a kraft cook can be fractionated, making it possible to collect a mixture that is rich in terpenoids, including abietic acid (Strazdins 1989; Lee et al. 2006). Abietic acid is a multi-ring compound. It is generally hydrophobic, except that it contains a carboxylic acid group. Most rosin used in papermaking has been partially "fortified" by treatment with either maleic or fumaric anhydride (Strazdins 1977). Fortification introduces two more carboxyl groups, after reaction with water. The carboxyl groups appear to facilitate either formation of a stable soap and more stable emulsions (Davison 1975). Fortification also inhibits crystallization of rosin products. Best results usually are obtained when only a small proportion of the abietic acid molecules are fortified (Eklund and Lindström 1991). Before forming an emulsified product, a slightly saponified mixture of partially fortified rosin is heated above its melting point.

The somewhat uncontrolled manner in which rosin soap size becomes precipitated (Strazdins 1977, 1981, 1984), and also the relatively high melting point of the aluminum

rosinates that form (Strazdins 1981) have been cited to help explain the relatively inefficient nature of this traditional sizing technology. Reaction of rosin soap and alum has been shown to yield mixtures of aluminum diresinate and free rosin (Davison 1975; Eklund and Lindström 1991). Sizing performance sometimes can be improved by adding coordinating ions such as citric acid, which lowers the melting point of the size particles (Strazdins 1981). If the paper mill's process water is hard, containing a relatively high level of calcium or magnesium, these ions can cause premature agglomeration of the rosin soap without significant contribution to water resistance (Strazdins 1977). To avoid this, papermakers often add aluminum compounds to the system before the rosin, even in the case of soap sizing. It has been reported that esterified rosin products (see later) are less sensitive to water hardness and other issues affecting electrostatic inter-actions during rosin sizing (Nitzman and Royappa 2003). Though rosin is the best-known product for soap sizing, the soaps of other materials such as fatty acids (Eklund and Lindström 1991, Shimada et al. 1997), and hydrolyzed ASA (Hatanaka et al. 1991) also are known to develop sizing upon the addition of alum or polyaluminum chloride (PAC).

Rosin dispersion products are capturing an increasing share of the rosin size market. When stabilized with a cationic polymer, rosin dispersion products offer advantages of self-retention onto fiber surfaces, lower melting points compared to precipitated soap size particles, and tolerance of somewhat higher pH values (Ehrhardt and Gast 1988; Lauzon 1997).

Self-sizing

Clues to the mechanisms involved in rosin sizing can be found in a phenomenon known as "self-sizing." Especially in the case of paper and paperboard made under acidic conditions from relatively high-yield fibers, the paper can gradually develop water-repellency over time, even without the addition of rosin (Galvin 1988; Hodgson and Ness 1999). Such uncontrolled hydrophobicity can become a serious problem, as in the case of corrugating medium, which needs to be sufficiently absorptive in order for gluing to be effective (Galvin 1988).

The role of wood extractives in self-sizing is shown by the fact that solvent extraction of pulp, before papermaking, can eliminate the effect (Swanson and Cordingly 1956; Soteland and Loras 1976). Swanson and Cordingly (1956) and Swanson (1978) proposed that self-sizing occurs as a result of vapor-phase diffusion of extractable materials during storage of paper. Sizing was observed in untreated sheets that were heated in sealed tubes, adjacent to wood pitch samples (Swanson and Cordingly 1956). Alum appears to accelerate self-sizing by providing anchoring sites at the paper surface, upon which resin acid and fatty acid molecules can become anchored and oriented (Swanson and Cordingly 1959; Aspler et al. 1985; Hodgson and Ness 1999). The fact that self-sizing becomes more rapid at high temperatures, for instance during the gradual cooling of a freshly-made roll of paper (Hodgson and Ness 1999), is consistent with these suggested mechanisms. One practical way to combat self-sizing effects is to add a surfactant to the paper (Aspler et al. 1985).

Though rosin size products ordinarily are not considered to be "reactive", there is evidence that, given sufficiently high temperature and time, the carboxyl groups on rosin can form esters with the hydroxyl groups on fiber surface (Swanson 1978; Zhuang et al.

1997; Hodgson and Ness 1999; Ness and Hodgson 1999). Such ester-bound rosin cannot be extracted. Under ordinary conditions of paper drying, such covalent bonds are not expected to play a major role.

Given the relative non-reactivity of rosin products, in comparison to ASA and AKD already described, it is perhaps surprising that both rosin dispersions and rosin soap products tend to be intolerant of very high temperatures within the paper machine system (Marton 1989). In the case of dispersed free-acid rosin products, there are two likely explanations. First, increasing temperatures above about 50 $^{\circ}$C can make the particles excessively tacky, resulting in agglomeration and less uniform distribution within the paper. Second, the higher temperature itself, as well as the resulting more liquid-like state of the rosin, will tend to speed up undesired conversion of the free acid to the soap form, which requires pH values below about 5 to react efficiently with alum (Marton 1989). In the case of soap sizing, the effect may be related to agglomeration, leading to increasing sizes of precipitated aluminum rosinate particles, again leading to inefficient coverage of the paper surface (Strazdins 1977).

Mordants for fixing and orienting adsorbed rosin molecules

If one excludes conditions so vigorous as to produce ester bonding, as just cited, then it is generally agreed that effective rosin sizing requires that a strongly positively charged species be present to anchor and orient molecules of rosin. In other words, there needs to be a mordant. Aluminum sulfate, or "papermaker's alum" is well known as an inexpensive and effective mordant for rosin sizing, especially in a pH range between about 4 and 5.5 (Back and Steenberg 1951; Strazdins 1977). It has been shown that aluminum species adsorb mainly on carboxylated sites at the fiber surface, thereby providing anchoring sites for rosin, which becomes distributed over the surfaces as paper is dried (Kitaoka et al. 1995). Alum-induced sizing appears to involve coordination-type bonds (Hodgson and Ness 1999). This assertion is supported by the fact that rosin sizing can be defeated by aluminum-complexing ions (Chen and Biermann 1995). Recent research has shown that alum is just one of many possible mordants. In Table 2 these candidate materials are listed roughly in order of the pH ranges in which the added materials have been found to function best in the promotion of rosin sizing.

Although Table 2 shows a pH range up to about 7.5 in the case of poly-aluminum chloride (PAC), such high pH values tend to convert aluminum ionic species to neutral alum floc, Al(OH)$_3$. Rosin acid molecules are expected to react with aluminum products attached to fiber surfaces as they become distributed during drying of the paper (Ehrhardt 1987; Marton 1989). However, the neutral species of alum are not expected to be very effective for retaining rosin particles when paper is being formed (Poppel and Bobu 1987). Thus, when paper technologists want to employ rosin products and aluminum products at neutral to weakly alkaline conditions, it makes sense to minimize the length of time that the aluminum product is in contact with the furnish (Ehrhardt and Gast 1988). Alternatively, some researchers have investigated sizing strategies involving pre-mixing of PAC or other aluminum products with rosin (Liu 1993; Peck and Markillie 1994; Zou et al. 2004), and then adding the mixture to the fiber furnish.

Table 2. Chemicals Having Ability to Act as Mordants for Rosin Sizing		
Type of Mordant	**Most Favorable pHs**	**Literature References**
Aluminum sulfate	4 – 4.5 (soap sizing) 4.5 – 5.5 (dispersed rosins)	Back and Steenberg 1951; Strazdins 1977
Poly-aluminum Chloride (PAC)	5 – 7.5	Traugott 1985; Isolati 1989; Liu 1993; Chen et al. 2001
Metals that form hydroxides	Depends on the metal	Strazdins 1963; Subramanyam and Biermann 1992; Zhuang and Beirmann 1995
Poly-ethyleneimine (PEI)	Near-neutral	Li et al. 2003; Hartong and Deng 2004
Linear polyamines	Near-neutral	Wu et al. 1997
Cationic amides of low charge density	Neutral – weakly alkaline	Wang and Tanaka 2001

With respect to inorganic ions, as mordants, Zhuang and Biermann (1995) observed that the most efficient rosin sizing tended to be achieved near to the pK_a value of the species under consideration.

In the case of the amine-type polymers listed in Table 2, the published evidence suggests that the sizing mechanism may involve some formation of covalent bonds between rosin molecules and the polymer (Hartong and Deng 2004). The mechanistic role of cationic polymers is somewhat hard to pin down, however, since the same additives can play a significant role in retaining the size particles as the paper is being formed (Norell et al. 1999). Similarly, Hedborg and Lindström (1993) showed that efficient rosin sizing could be achieved under neutral conditions by use of a retention aid system that contained colloidal aluminum compounds as one of the additives.

Sizing contribution of non-bound species

Recent work showed, in the case of sizing with dispersed rosin, that much of the sizing agent remained in an unreacted, free-acid form, even after the paper was dried (Kitaoka et al. 1997). In apparent contradiction of the theory that aluminum in the sheet ought to be binding rosin to the paper surface (Marton 1989), no evidence of aluminum rosinate formation was found (Kitaoka et al. 1997). Such observations provide a lead-in to the topic of esterified rosin sizing agents. By esterification, many of the carboxyl groups on rosin essentially become blocked, no longer able to participate in interactions with any of the mordant materials just described. Nevertheless, esterified rosins have extended the range of rosin sizing to somewhat higher pH values (Fallmann and Bernardis 1997; Iwasa 1999; Ito et al. 1999; Fischer 1999; Nitzman and Royappa 2003; Liu et al. 2004). A likely explanation for these effects is that a degree of ionic binding involving far lower than 100% of the hydrophobic molecules may be sufficient to achieve a stable sizing effect. Thus, it is not surprising that superior results often are achieved with optimized mixtures of esterified and conventional partially fortified rosin products (Iwasa 1999), only the latter of which have a mechanism that allows strong anchoring of the molecules. In theory, the bound molecules will tend to hold the unbound molecules in place by hydrophobic association. Such a mechanism also can help explain why rosin esters, by themselves, sometimes show almost no sizing effect (Wang et al. 1999).

Case 4: Polymeric Sizing Agents

Though copolymers of various sorts are more often used at the size-press of paper machines to impart water repellency (Batton 1995; Garrett and Lee 1998), their use at the wet end can provide us with further insights, especially when contrasted with the ASA, AKD, and rosin sizes just discussed. Polymeric wet-end hydrophobic agents can include ethylene-acrylic acid copolymers (Finlayson et al. 1996; Wang et al. 1997; Hodgson 1997), styrene-maleic-anhydride (SMA) copolymers (Batton 1995), when used at the wet end, cationic styrene copolymers (Ono and Deng 1997; Yang and Deng 2000), derivatized acrylamides (Takai et al. 1997), and derivatized starch (Yang et al. 1999). Products having cationic groups (Ono and Deng 1997; Yang and Deng 2000; Valton et al. 2003) generally can be efficiently retained during papermaking without depending on other additives. By contrast, anionic copolymers are used in sequence with cationic additives such as alum (Takai et al. 1997; Wang et al. 1997) or cationic copolymer retention aids (Finlayson et al. 1996). Polymeric sizes tend to be less efficient on a mass or cost basis, compared to the amounts of ASA or AKD to achieve a given level of hydrophobicity. On the plus side, they have potential to offer a more precise and reliable gradation of sizing, and they don't suffer from any size-reversion issues. When properly formulated, polymeric sizing agents can have a long shelf-life (Finlayson et al. 1996).

Accounts of sizing with polymeric materials provide various examples in which it is clear that distribution over the fiber surfaces tends to be patch-like, or at least non-uniform on a molecular scale. For instance, Carceller and Juppo (2005) observed that the amphiphylic copolymers they studied tended to form 30 nm particles. The dried film resulting from such treatment showed a network pattern. Garnier et al. 2000 showed that SMA macromolecules tend to self-associate, especially under pH conditions such that about half of the carboxyl groups were in their ionic form. Others have achieved sizing effects with materials consisting of latex-like particles or microaggregates (Ono and Deng 1997; Yang and Deng 2000; Finlayson et al. 1996).
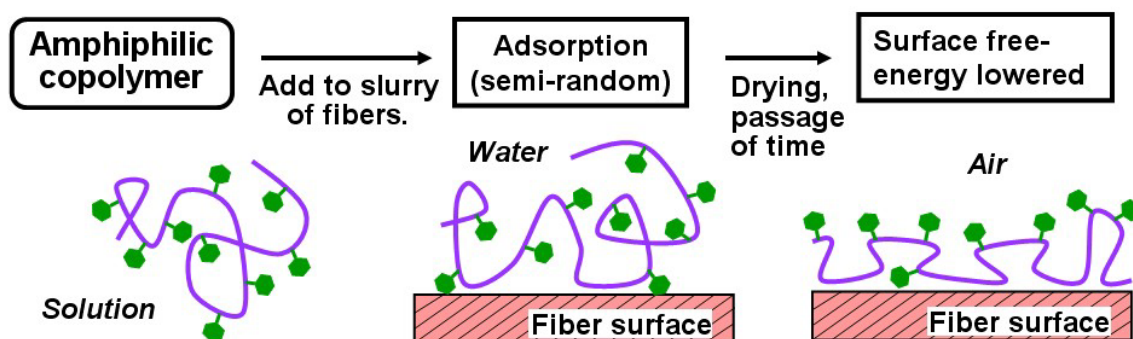

Fig. 4. Concept of rearrangement upon drying of amphiphilic copolymer, such that more hydrophobic groups end up facing the air phase and more hydrophilic groups end up facing the fiber

Although copolymeric sizing agents cannot migrate through the vapor phase or as monomeric films, it is reasonable to expect that they change their molecular conformations when paper is dried. As illustrated in Fig. 4, it would be expected that water-hating groups would tend to orient themselves facing outwards from the paper surface during

the final stages of drying, thus decreasing the interfacial free energy of the system (Garnier et al. 2000). Garrett and Lee (1998) suggested that the copolymers may be able to gradually rearrange their conformation upon exposure to water, such that an increasing proportion of hydrophilic groups face the aqueous phase. Yasuda et al. (1995) confirmed such rearrangement by ESCA analysis for another type of amphiphilic copolymer. Such conformational adjustments may provide a mechanism by which to achieve intermediate levels of resistance to fluids in a reliable way.

ADDING UP THE EVIDENCE

Based on work cited in the preceding section it is possible to claim general support for the hypothesis proposed earlier. Thus, the hydrophobic active ingredient of the sizing agent must contain a hydrophobic group, it must become well dispersed, it must remain in its active form up to a critical point in the papermaking process, it must be retained efficiently in the wet-web of paper, it must become well distributed on the outer surfaces of the paper by the time it is dried, and individual molecules of the sizing agent must become anchored and oriented in order to achieve a stable and efficient sizing effect. However, sizing systems are subject to a variety of interferences, competing reactions, and unique properties of the sizing molecules. Some of these complicating factors will be highlighted here.

Sizing Can Be Blocked or Covered
Studies of the fundamentals of paper sizing sometimes may be misleading in cases where the systems under investigation are artificially "clean." Various studies have shown that solvent-extractable materials in papermaking furnish can adversely affect sizing treatments (Johansson and Lindström 2004a; Liden and Tollander 2004). Some of the evidence suggests that anionic colloidal material, such as extractives, can interfere with the retention of sizing agents during papermaking (Mikkonen and Eklund 1998). In other cases, surface-active materials in the furnish just act as wetting agents, presumably because they lack a mechanism that would anchor them in position, orienting the molecules in the manner of an effective sizing agent (Moyers 1992; Brinen and Kulick 1995, 1996; Boone 1996).

In other cases extractives on the surfaces of paper appear to block sites that otherwise could become occupied by molecules of a sizing agent (Zeno et al. 2005; Avitsland et al. 2006). A similar phenomenon may explain the adverse effect of aluminum sulfate on AKD sizing (Kamutzki and Krause 1983). Moderate amounts of alum decreased the effectiveness of AKD, despite the fact that retention efficiency of the sizing agent was greatly improved. The effect suggests that the fiber surfaces became covered by a film of oligomeric hydrated aluminum species (Strazdins 1984), and that AKD was not able to form covalent bonds to such species. A similar explanation can be offered to explain the difficulties of obtaining stable sizing in the presence of high levels of PCC filler (Patton 1991; Moyers 1992; Bartz et al. 1994; Esser and Ettl 1997).

It Doesn't Take Much

      Another take-away message from the published literature, especially as it pertains to ASA and AKD, is that very little hydrophobic material is required, if only it could be distributed in an ideal way and reacted at 100% efficiency. As discussed earlier, researchers have achieved sizing effects with as little as 0.006 to 0.01% of sizing materials remaining in paper after solvent extraction (Roberts and Garner 1985; Dumas and Evans 1986; Lindström and Söderberg 1986). Advanced methods are required even to quantify the presence of sizing agents in paper, let alone determine the manner in which they are bound (Dart 1990; Sundberg et al. 1999; Vrbanac et al. 1999; Yano et al. 2000; Odermatt et al. 2003). Davison (1986) estimated that it takes about 1 mg of sizing agent per square meter of surface to form half of a contiguous monolayer. If one assumes that the surface area of dry paper lies within 1-3 m^2/g, it follows that a loading of 0.05 to 0.15% sizing agent in paper ought to be enough to size paper. It is reasonable to expect less than a molecular layer of sizing agent to be effective, due to the fact that a molecule attached at one end can be expected to "sweep" a larger area than it occupies at any instant (Lindström and Söderberg 1986).

It Doesn't Have to be Uniform

      The effectiveness of low levels of sizing agents also can be attributed to hysteresis effects, *i.e.* the reluctance of a liquid meniscus to advance across rough, porous, or heterogeneous surfaces (von Bahr et al. 2004). Matsuyama et al. (2006) found support for the theories of Cassie and Baxter (1944), showing that it is difficult for a meniscus of water to advance across a dry, porous surface. These researchers were able to achieve a high degree of hydrophylicity by covering just 20% of a hydrophilic substrate with hydrophobically modified colloidal gold particles. The study also demonstrated the validity of early work by Wenzel (1936), related to the equilibrium contact angles of fluids on surfaces having a very fine scale of roughness. Wenzel's main conclusion can be summarized by stating that fine-scale roughness can greatly increase the contrast between wettable and hydrophobic surfaces, and one can expect a relatively sharp transition from one state to the other at a certain level of treatment with a hydrophobic agent. All of the effects mentioned above help to explain why significant sizing often is observed only after the amount of sizing agent has reached a threshold, whereas further increases in size dosage often yield sharp increases in fluid resistance (Dumas and Evans 1986; Wasser 1986; Crouse and Wimer 1991; Esser and Ettl 1997; Johansson and Lindström 2004b; Isogai and Morimoto 2004).

      On a micrometer scale, various studies have shown non-uniformity in the surface distribution of sizing agents. Such observations have been reported especially in the case of rosin sizing (Davison 1975; Strazdins 1981; Ozaki and Sawatari 1997; Wang et al. 2000), and excessively non-uniform coverage has been correlated to inefficient sizing (Lee 1936; Strazdins 1981). In the early work by Lee (1936) the most efficient sizing with rosin soap was achieved when the size particles were the smallest, achieving a better distribution. More recent work shows, however, that microscopic studies may miss an important part of the story; Ozaki and Sawatari (1997), using electron probe micro-analysis (EPMA), detected an uneven distribution of rosin. However, the same samples, when studied by time-of-flight surface ionization mass spectroscopy (TOF-SIMS)

revealed a molecular layer of rosin covering essentially the whole surface. Related results were obtained by Shen et al. (2001) in the case of AKD sizing. Dynamic contact angle analysis of AKD-sized fibers revealed a high degree of heterogeneity. However, steady contact angles and a high degree of hydrophobicity were observed after solvent extraction to remove unbound material.

Airborne Distribution Supplements Partial Spreading

Vapor-phase transport of sizing agents is relatively easy to demonstrate by solvent-treatment of one sheet, and then placing the treated sheet in a foil wrapper with a stack of untreated sheets. In the case of reactive sizing agents such as ASA, AKD, and stearic anhydride, sizing effects develop in untreated sheets, even when they are separated by several layers from the treated sheet. Vapor-phase transport of various compounds related to sizing agents have been demonstrated (Davis et al. 1956; Swanson 1978; McCarthy and Stratton 1987; Back and Danielsson 1991; Yu and Garnier 1997; Shen et al. 2001; Gess and Rende 2005).

Though the traditional explanations for sizing effects often assume melting and spreading of droplets of sizing agents on the solid surfaces of paper (Davison 1986), we have seen earlier in this review that most evidence suggests rather limited spreading of liquid sizing agents (Seppänen and Tiberg 1999; Garnier et al. 1999; Garnier and Godbout 2000; Lindfors et al. 2005). Likewise, the spreading of monomolecular "precursor" films appears to be rather inefficient (Garnier and Godbout 2000). Evidence for and against a vapor-phase mechanism of size distribution is sometimes clouded by competing reactions. Thus, attempts to find evidence for AKD migration through the vapor phase sometimes show only the hydrolysis product on the target surfaces (Akpabio and Roberts 1987; Hutton and Shen 2005).

Non-bound Materials Can Contribute

Another general conclusion that can be drawn from published literature already cited is that although unbound hydrophobic species *can* contribute to sizing, as long as conditions are favorable, these contributions tend to be supplemental, rather than central to efficient sizing practices. As was noted, such contributions can depend strongly on having a certain amount of bound sizing agent present (Lee and Luner 2005). Lindström and Söderberg (1986a) obtained an especially convincing set of data, showing very high correspondence between the amounts of chemically bound AKD and the degree of water hold-out, irrespective of the presence or absence of other chemical species related to AKD. Some researchers have described unbound hydrophobes as inefficient sizing agents, compared to those molecules that are properly anchored and oriented (Lindström and Söderberg 1986; Bottorff and Sullivan 1993). Other research found little or no contribution to sizing effects due to unreacted AKD (Karademir 2002).

To present a balanced picture, some researches have noted cases where the contribution of unbound hydrophobic materials appeared to be important. Significant contributions to sizing have been reported for unreacted AKD (Lindström and Söderberg 1986; Colasurdo and Thorn 1992), as well as unbound oligomers of AKD (Bottorff 1993; Bottorg and Sullivan 1993). Colasurdo and Thorn (1992) demonstrated the sizing effect of unreacted AKD by showing cases in which solvent extraction made the paper wettable

again. In the case of rosin, Kitaoka et al. (1997) estimated that 80% of the added rosin remained in an unchanged, free-acid chemical form, following sizing with a dispersed rosin product. Subsequent solvent extraction eliminated the sizing effect.   Aluminum rosinates were not detectable, despite the fact that without aluminum salts in the system, no sizing was observed.

PATHS TOWARDS HIGHER SIZING EFFICIENCY

Major increases in the efficiency of sizing systems are possible, relative to today's technology, at least in theory. The rather inefficient nature of the available sizing technologies has been documented in earlier sections of this article. Though there is no assurance that the theoretical limits of sizing efficiency ever can be achieved in practice, one can point to a number of variables that will need to be considered. Among these are the design of the hydrophobic group, the nature of the anchoring group, and the sizing agent's vapor pressure as a function of temperature. For sake of discussion, let us assume that issues related to retention of the sizing agent and avoidance of the effects of interfering substances, such as surface-active materials, can be addressed by known technologies, such as pulp washing and the use of retention aid systems.

With respect to the design of hydrophobic groups, both the size and the shape can be expected to be important. Various studies have shown increasing effectiveness of sizing agents with increasing chain length of alkyl groups, assuming that curing conditions are sufficient to achieve good distribution and reaction (Roberts et al. 1993; Smith 1999). A somewhat bulky, centrally-attached hydrophobic group, as in the case of rosin (Shimada et al. 1997) or isomerized ASA (Roberts et al. 1993; Smith 1999) can be expected to protect the bond by which the sizing molecule is attached and oriented. An isomerized alkenyl group, in the case of ASA, also is expected to hide the extra carboxylate group that results during the formation of an ester bond (Roberts et al. 1993). However, the currently available sizing agents do not come close to exhausting the possible kinds of hydrophobic groups that could be used in the future to better meet the needs of end-users. For example, it may be possible to achieve superior adhesion of inks and toner particles to sized paper (Borch 1986), if a reactive sizing agent were prepared with a hydrophobic group related to either styrene or rosin.

Researchers hoping to find a more effective reactive group, in comparison to ASA or AKD, face considerable challenge. Many alternative reactive chemistries have been considered, but none of them have achieved long-term commercial success (Dumas 1981; Jing et al. 1998). Not only must the active material be able to form a stable attachment to fiber surfaces, but it also has to resist adverse side reactions during storage and during production of the paper (Robert 1997). Work by Rossall and Robertson (1975) suggests that the reactivity of sizing chemicals towards hydroxyl groups at the fiber surface and towards water might be fine-tuned by varying the size of anhydride rings and by judicious use of conjugated double bonds associated with those rings. Another possible approach would be to encapsulate sizing agents, such that the active ingredient is released only after most of the moisture has been dried from a sheet of paper (Hunkeler 2006).

Relative to the importance of the subject, little published work has touched upon optimization of the partial pressure of sizing agents as a function of temperature. Adverse effects of excessively volatile sizing agents include deposits in the hoods of paper machine drier sections (Gess and Rende 2005) and the concurrent inefficiencies. At the other extreme, AKD products are typically about 1.5 times the molecular mass of an ASA molecule. This circumstance may help explain why over-drying of paper is often required to achieve sizing ahead of a size press (Roberts 1997), and why full AKD sizing often is not achieved until after storage of paper rolls. An AKD product having a single alkyl chain might come closer to the optimum in terms of vapor pressure, though someone needs to figure out what to do with the other end of the molecule. This question, as well as a great many questions related to addition strategies and interactions with other wet-end additives can be expected to keep paper technologists occupied for a long time to come.

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