Preferred citation: J.S. Aspler, N. Chauret and M.B. Lyne. Mechanism of self-sizing of paper. In **Papermaking Raw Materials**, *Trans. of the VIIIth Fund. Res. Symp. Oxford, 1985*, (V. Punton, ed.), pp 707–727, FRC, Manchester, 2018. DOI: 10.15376/frc.1985.2.707.

MECHANISM OF SELF-SIZING OF PAPER

J. S. Aspler, N. Chauret*, and M. B. Lyne+
Pulp and Paper Research Institute of Canada
570 St.John's Boulevard, Pointe Claire, P.Q., Canada HR9 3J9

ABSTRACT

Investigations on the self-sizing of a pure cellulose paper show that surfactant acts to prevent self-sizing by solubilizing fatty acid molecules and forming a physical barrier to chemical bond formation between cellulose and fatty acid molecules. The acceleration of self-sizing by alum has a mechanism similar to that of conventional rosin-alum sizing: the formation and polymerization of aluminum soaps on the fibre surface. It is suggested that the reaction between cellulose hydroxyl groups and aluminum soaps, as proposed in the literature, is not likely. Instead, material that is not solvent-extractable is either extensively polymerized or reacted with residual carboxyl groups on the fibre surface.

INTRODUCTION

The paper industry today is making increased use of mechanical and semi-chemical pulps containing natural resin and fatty acids, and of recycled fibre containing surface active and/or hydrophobic contaminants. This practice results in papers with surface chemical properties different from those commonly seen in the past. At the same time, the industrial application of aqueous liquids to paper is increasing. They are used in printing, where, in offset lithography (the most widely used technique), aqueous fountain solutions are applied to paper in the non-image areas, and water-containing ink emul-

---

* Summer student from Université de Montréal, 1984

\+ Now with International Paper Company, Corporate Research Centre, Tuxedo Park, NY, 10990 sions are applied to the image areas. Water-based inks are also finding increasing use in other printing methods, notably in the flexographic printing of newspapers, and in ink jet printing. Aqueous adhesives are being increasingly used in the packaging field, and water-based materials are also applied to paper at high speed in the pigmented coating of paper. The high-speed wetting of paper and sorption of aqueous liquids is thus becoming more critical at a time when the surface chemistry of paper is becoming more complex.

In this paper, the role of alum and surfactants in both augmenting and preventing self-sizing is explained from the results of pyrolysis of experimentally treated and aged paper samples, and gas chromatographic and infrared analysis of extractives from these same samples.

Surfactants and Paper

Papermakers have added surfactants to paper for many years. Reasons for this addition may include fines and pitch retention, improved tactile softness, and the facilitation of pulping and beating. Touchette and Jenness [1] examined the effect of the electrical charge of the surfactant molecule on drainage and physical strength properties of sulphite pulp. Cationic surfactants had the greatest effect, since they are held more strongly to the anionic surface of cellulose, and caused decreased fibre bonding manifested in increased tear strength and decreased breaking length and burst strength. This phenomenon is used commercially to improve the softness of tissues and similar products. Nonionic surfactants have a similar but smaller effect on breaking length and burst than cationic surfactants, while anionic surfactants have the opposite effect. In addition to the direct effect of the surfactant electrical charge on bonding, there is a general tendency for surfactants to reduce the surface tension forces that pull fibres together during drying, thereby decreasing the bonded area. Wet-end addition of surfactants has been reviewed by various authors [2-4].

However, increasing the rate of sorption of water and aqueous liquids by deliberately applying surfactant to paper has been little pursued. In 1954, Nicolaysen and Borgin [5] reviewed the literature on the use of surfactants in paper to that date, and also showed that surfactant could be used to increase the wettability of pure cellulose fibres previously rendered hydrophobic by the addition of wood resins. Surfactants in aqueous solution added as aerosol sprays to the surface of paper may increase the rate of water sorption. In a recent patent [6], a surfactant applied as a spray was used to improve the wettability of a battery separator made mainly of a synthetic fibre furnish. Field [7] investigated the requirements for highly absorbent fluff-type pulps. He noted that when the surfactant is sprayed onto the pulp during drying, less surfactant is lost than in wet-end addition, but that the debonding effect of wet-end addition of cationic surfactants is obviated in spray addition onto the already-formed sheet.

In earlier work by the present authors [8], a large number of commercially available surfactants was applied to newsprint, and the change in the dynamic sorption of water was monitored. It was found that at constant weight of added surfactant, the single most important factor in improving the wettability of the paper was the molecular weight of the surfactant molecule - that is, more small molecules per unit area were of greater benefit than fewer large molecules. Structure and electrical charge were found to have negligible influence on wettability improvement, and surfactants applied as aqueous dispersions were less effective than those applied as solutions.

Self-Sizing

The self-sizing of paper is a phenomenon that has been known for a long time, but little studied. Products containing resin and fatty acid materials may, with time or heating, develop water-repellence. This may create problems in any product where the rapid and uniform sorption of water is important. On the other hand, deliberate promotion of self-sizing may give a certain amount of water repellence at low cost.

R.E. Swanson [9] has suggested that vapour phase migration from resin ducts and ray cells is important in self-sizing. He found that chemisorbed material is more efficient at causing self-sizing, since after heating a regenerated cellulose film with stearic acid, he observed an infrared absorption band assigned to cellulose stearate. Takeyama and Gray [10] showed that a pure cellulose paper that had been heated with stearic acid remained hydrophobic even after exhaustive solvent extraction. The hydrophilic nature of the paper could be restored by immersion in a solution of sodium methoxide. Since quantitative gas chromatographic analysis showed the recovery of methyl stearate equivalent to less than one monolayer on the paper, Takeyama and Gray concluded that this small amount had been bonded to the paper as cellulose stearate, and could be debonded only by a strong base like sodium methoxide.

Some years earlier, J.W. Swanson [11] showed that papermakers' alum contributes to the efficiency with which self-sizing occurs. The importance of alum in rosin sizing has, of course, been known for many years, and the literature contains several thousand references on the subject [e.g., 12-15]. Within the North American paper industry it is common knowledge that addition of alum to the wet end of the paper machine will give a somewhat more self-sized sheet.

Nevertheless, self-sizing and the role that alum plays have been little studied. In earlier work by the authors [16], it was shown that newsprints containing alum self-size much more rapidly than those that are alum-free. Immediate (although partial) self-sizing developed after alum had been added to alum-free newsprint by immersion or spray. Permanent sizing developed after the sample had been heated to 105°C. Some of these results are shown in Table 1. The temperature

Sample	k_a, mL m^{-2} $sec^{-\frac{1}{2}}$	
	Dried at 23° C	After accelerated aging
Newsprint,		
initial [Al] = 0	94	67
- plus 70 ppm added Al	72	29
- plus 640 ppm added Al	39	13
Newsprint,		
initial [Al] = 70 ppm	142	32
Newsprint,		
initial [Al] = 640 ppm	150	8

Table 1. Effect of Changing Aluminum Content on Dynamic Sorption [16].

and pH dependence of the self-sizing suggested that the process occurs by a mechanism analogous to that of conventional rosin-alum sizing. At the same time, surfactant added to the paper as a spray prevented self-sizing in the presence or absence of alum. Extraction and wettability tests suggested that the surfactant prevents and does not simply mask self-sizing.

Although surfactants have been added to paper for reasons other than that of increasing wettability, there is a growing awareness that the presence of surfactant will impede self-sizing. Collins and Mulyk [17], in a discussion of the pulping of a problem wood species (aspen), pointed out that surfactant added to NSSC liquor reduced self-sizing. J.W. Swanson [18] has observed that the benefits of surfactant addition to NSSC pulps are not always seen with green liquor semi-chemical pulps. Others, such as Soteland [19], noted that papers buffered to a slightly alkaline pH were free from self-sizing, presumably because of the formation of soluble sodium soaps. The main object of the present research was to clarify the mechanism by which alum and surfactants affect the self-sizing of papers containing resin and fatty acids. Related to the deliberate application of surfactants to paper is the high speed sorption of surfactant-containing aqueous liquids such as offset fountain solutions. Although a full discussion is beyond the scope of the present paper, a brief description of this related work is given in Appendix I.

EXPERIMENTAL

Self-Sizing Experiments

The mechanism of self-sizing was investigated by applying stearic acid, alum, and surfactant to Whatman No. 1 chromatographic paper (a low ash, pure cellulose paper). Internal reflectance infrared spectroscopy was done on additive-free regenerated cellulose film which had been Soxhlet extracted for 36 hours in acetone. All samples were stored in sealed bags in a freezer when not in use.

Stearic acid of 99.1% purity (n-octadecanoic acid; Sigma Corp.) was used as received. Gas chromatographic analysis showed 0.9% n-hexadecanoic acid as impurity. Reagent grade alum $\left(Al_2(SO_4)_3 \cdot 18\ H_2O\right)$ was used as received. Triton X-100 was used in this part of the work since, aside from being a common industrial surfactant, it also has a structure that is typical of a large number of other common commercial surfactants.

Reagents were applied to the paper by immersion in solutions of appropriate concentration, followed by blotting and air-drying. High purity HPLC (high pressure liquid chromatography) grade solvents were used at all times. Stearic acid was applied from acetone solution, and alum and Triton X-100 from aqueous solution. For accelerated aging, samples were wrapped in aluminum foil and placed in an oven at 105°C for 24 hours. Details of quantitative analytical techniques are given in Appendix II.

Pyrolysis Gas Chromatographic Measurements

Paper samples milled through a 60 mesh screen were pyrolyzed at 650°C, and the degradation products were immediately introduced into a gas chromatograph equipped with a capillary column. The initial column temperature was 200°C, and the GC oven was programmed to increase to a final temperature of 275°C by the end of the run.

RESULTS AND DISCUSSION

There were several important questions left unanswered from the previous work [16]. The most important of these were the question of how surfactant prevents self-sizing, and how alum acts to accelerate it. Four basic combinations were examined: pure cellulose paper plus stearic acid (a repeat of the work done previously [9,10]); cellulose, stearic acid, and alum; cellulose, stearic acid, and surfactant; and cellulose, stearic acid, alum, and surfactant.

Pure Cellulose Paper and Stearic Acid

As expected, stearic acid physically adsorbed onto pure cellulose gave a modest increase in the water drop absorption time (from 1 to 60 seconds) (Table 2). Solvent extraction returned the paper to its original hydrophilic state (drop time = 1 second) while yielding 1.4% stearic acid by weight. (It is assumed that, since the paper was extracted immediately after the stearic acid had been added, the amount extracted is the full amount deposited.) The complete restoration of hydrophilicity is indicative of fatty acid that is only physically adsorbed onto the fibre surfaces, this behavior being similar to that seen in fresh, unaged mechanical pulps [16].

	Dried at 23°C	After accelerated aging, 24 hours, 105°C
Water drop time, sec	60	>3000
Acetone extractives, ±0.1%	1.4	1.2
GC analysis of acetone extractives, % stearic acid	100	100
IR analysis of acetone extractives, cm^{-1}	1700 (s)	1700 (s)
Water drop time after acetone extraction, sec	1	>3000
* $CHCl_3$ extractives, %	0	0
Water drop time, sec	1	>3000
* Benzene/ethanol extractives, %	0	0
Water drop time, sec	1	>3000
* $NaOCH_3$ extracted, %	0	0.3
Water drop time, sec	1	1

IR absorption: s - strong.
* Extraction done sequentially on sample from previous step.

Table 2. Analytical Data for Pure Cellulose Treated with Stearic Acid

After accelerated aging of the paper at 105°C, the drop time became "infinite" (i.e., the drop evaporated without penetrating the paper). This is denoted as t > 3000 seconds. Solvent extraction did not reduce the water drop absorption time and yielded only 1.2% stearic acid. Analysis of the acetone-extracted material by gas chromatography showed pure stearic acid. The infrared spectrum of this extract confirms only the 1700 cm^{-1} absorption of pure stearic acid in its normal dimer form (Figure 1A).

As in the earlier work of Takeyama and Gray [10], treatment with sodium methoxide restored the paper to its original hydrophilic state, while yielding an additional 0.3% by weight of stearic acid. Presumably this stearic acid had been bonded to the cellulose as stearate. Internal reflectance infrared examination of a regenerated cellulose film that had been exhaustively solvent-extracted after heating with stearic acid showed the carbonyl absorption at about 1735 cm^{-1} assigned by Swanson to cellulose stearate [9]. Therefore, the results in this section confirm - using a different method of stearic acid application - the work of Swanson [9] and of Takeyama and Gray [10].

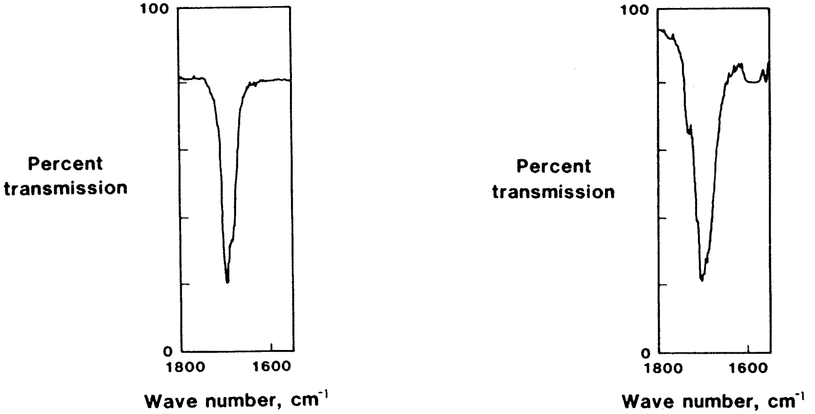

Fig 1—A. Infrared spectrum of stearic acid, as KBr pellet.
B. Infrared spectrum of chloroform extract from paper treated with stearic acid and alum after accelerated aging, as KBr pellet.

Pure Cellulose Paper, Stearic Acid, and Alum

Paper samples containing stearic acid from the previous experiments were immersed in dilute aqueous alum and air dried at 23°C overnight. As shown in Table 3, the water drop time increased significantly after room temperature drying. Given the ready formation of aluminum soaps between fatty acids and aluminum salts [20-22], a low molecular weight aluminum stearate complex that is more hydrophobic than pure stearic acid is likely to have formed - even under these very mild conditions.

	Dried at 23°C	After accelerated aging, 24 hours, 105°C
Water drop time, sec	1000	>3000
Al content of paper, parts per million	270	270
Acetone extractives, ±0.1%	1.4	1.2
Water drop time after extraction, sec	1	>3000
** $CHCl_3$ extractives, %	0	0
Water drop time, sec	1	>3000
*Al content of paper after extraction, ppm	270	160
*GC analysis of extract, %, stearic acid	100	94-100***
*IR analysis of extract, cm^{-1}	1700 (s)	1700 (s), 1735 (sh), 1600 (w)
** Benzene/ethanol extractives, %	0	0
Water drop time, sec	1	>3000
** $NaOCH_3$ extracted, %	0.007	0.4
Water drop time, sec	1	1

IR absorption: s - strong; sh - shoulder; w - weak.

* For these measurements, a fresh paper sample was used which had not previously been acetone extracted.

** Extraction done sequentially on sample from previous step.

*** See text.

Table 3. Analytical Data for Pure Cellulose Treated with Stearic Acid, and Alum

Solvent extraction yielded 1.4% of material and returned the paper to its initial hydrophilic state. Gas chromatographic and infrared analysis of the extract showed recovery of pure stearic acid. The extraction for GC and IR analysis was done on a sample that had not previously been acetone extracted.

Alum addition and room temperature drying followed by accelerated aging at 105°C caused complete hydrophobicity of the slightly hydrophobic paper containing physisorbed stearic acid. Solvent extraction with acetone, chloroform, and the 2:1 azeotrope of benzene and ethanol yielded 1.2% by weight of extract. The hydrophobicity of the paper, however, was not decreased by this exhaustive solvent extraction.

The infrared spectrum of the chloroform extract showed (Figure 1B), in addition to the stearic acid dimer absorption at 1700 cm^{-1}, a shoulder at 1735 cm^{-1} and a new, weak absorption at 1600 cm^{-1}. These are indicative of an extracted aluminum stearate, as the 1600 cm^{-1} absorption is common in metal carboxylates. The 1735 cm^{-1} absorption, while difficult to isolate from the stronger 1700 cm^{-1} absorption, could be that of the stearic acid monomer often found with aluminum stearates [20]. Internal reflectance IR could not be used to look for metal carboxylates on the surface of regenerated cellulose film due to the presence of an overlapping cellulose absorption band.

The difference in the aluminum content of the paper before and after solvent extraction is consistent with aluminum stearate making up between 5 and 10% of the extracted material. Gas chromatographic analysis of the diazomethane-derivatized extract showed it to be pure stearic acid, but direct injection of the extract into the GC with the addition of the internal standard but without derivatization yielded only 94% stearic acid. The infrared spectrum suggests the presence in the extract of a small amount of aluminum ester. This may have been saponified back to stearic acid in the presence of diazomethane, although there is no direct evidence for such a reaction.

Sodium methoxide treatment after exhaustive solvent extraction of the aged (heated) paper yielded 0.4% of stearic acid by weight, and returned the paper to its original water-absorbent state. Therefore, the self-sizing is likely aided by at least two forms of aluminum stearate. Before heating, there is rapid, reversible formation of a low molecular weight aluminum stearate that is more hydrophobic than pure stearic acid (water drop time of 1000 seconds vs. water drop time of only 60 seconds). As discussed later, the non-solvent extractable material that developed after heating is probably highly polymerized aluminum stearate, with the added possibility of having reacted directly with the fibre surfaces.

Pure Cellulose Paper, Stearic Acid, and Surfactant

As previously found with newsprint [16], the application of surfactant to the paper containing stearic acid did not merely mask but stopped self-sizing (Table 4). Gas chromatographic analysis of the 2.1% by weight of material solvent-extracted from the unaged paper showed 42% stearic acid and 58% surfactant. It is assumed that the weight and proportion of each in the extract from the unaged paper is identical to the amount originally added.

	Dried at 23°C	After accelerated aging 24 hours, 105°C
Water drop time, sec	20	15
Acetone extractives, %	2.1	2.1
Water drop time after extraction, sec	1	1
GC analysis of acetone extract, %, stearic acid	42	42
%, surfactant	58	58**
IR analysis of extract, cm^{-1}	1700 (s)	1700 (s), 1725 (s)*, 1750 (s)*

* New infrared absorption bands are those of oxidation products from ethylene oxide portion of surfactant molecule.

** Includes oxidation products.

Table 4. Analytical Data for Pure Cellulose Treated with Stearic Acid, and Surfactant

The aged paper yielded the same amount (2.1% by weight) of extract as the unaged paper. As the same amount (42%) of stearic acid was found in the extract after aging, there is no reaction between stearic acid and surfactant, within detectable limits.

The generally accepted mechanism for self-sizing under these conditions is the movement of fatty/resin acid molecules along the fibre surface, with a small number of chemical bonds formed between the hydroxyl groups of the cellulose and the carboxyl groups of the acids. Since we have calculated that the surfactant is present in about a four layer thickness on the fibres [23], it is likely that the hydrophobic material is solubilized by the surfactant so that it cannot move to, orient itself with, or react with the fibre surface.

Pure Cellulose Paper, Stearic Acid, Surfactant, and Alum

As shown in Table 5, in contrast to its effect on the surfactant-free paper (Table 3), alum added to paper containing both stearic acid and surfactant did not cause a major increase in the water drop absorption time. Accelerated aging of the paper caused virtually no increase in hydrophobicity and had no effect on the amount of material extracted. The little self-sizing that did develop was eliminated by solvent extraction.

	Dried at 23°C	After accelerating aging, 24 hours, 105°C
Water drop time, sec	15	60
$CHCl_3$ extractives, %	1.8*	1.8
Water drop time, sec	1	1
GC analysis of extract,% s. acid	64*	65
%, surfactant	36*	35**
IR analysis of extract, cm^{-1}	1700 (s)	1700 (s), 1725 (s),*** 1750 (s)***

* Total amount and proportion of materials added differ from Table IV and result from altering the order in which they were applied to the paper. This did not have any effect on the degree of self-sizing or the other analytical data.

** Includes oxidation products.

*** New infrared absorption bands are those of oxidation products from ethylene oxide portion of surfactant molecule.

Table 5. Analytical Data for Pure Cellulose Treated with Stearic Acid, Alum and Surfactant

Gas chromatographic and infrared analysis of the extract showed the same results as in the absence of alum: there was no change in the amount of stearic acid extracted after accelerated aging.

As suggested in the preceding section, surfactant may form a physical barrier to the movement of fatty acids and the formation of cellulose-fatty acid esters. But how does surfactant prevent self-sizing in the presence of alum? It seems certain that alum and stearic acid form polymerized aluminum stearate as part of the self-sizing process, and may also react to form mixed cellulose carboxyl-aluminum-fatty acid esters. If the surfactant forms a barrier to the formation of cellulose stearate in the absence of alum, it is also likely to act as a barrier to the reaction of an alum complex with cellulose in addition to solubilizing aluminum soaps.

The Nature of Stearic Acid on the Fibre Surface in the in the Presence of Alum

In conventional rosin-alum sizing, the formation of the size precipitate, its deposition on the fibres, and melting and spreading in the drying process are all reasonably well understood. Work in the past [12-15] has demonstrated that electrostatic attraction between the cationic size precipitate and the anionic cellulose fibres is the first, and perhaps the most important, step in sizing. The deposition and retention of the size precipitate on the fibres are also affected by factors such as Van der Waals interactions and non-cellulosic components of the fibre surface. There has never been a conclusive demonstration, however, of the chemical reaction between size precipitate and the fibre surfaces via an aluminum complex that has been proposed as the final step in sizing [24]. Although a discussion of the wet-end interactions between size and cellulose is beyond the scope of the present paper, conclusions can be drawn on the nature of stearic acid and alum once dried on the fibre surface.

Pyrolysis gas chromatography is a useful tool for looking at the relatively volatile components of a paper, and was expected to yield information on the nature of the aluminum stearate on the fibre surfaces. While this proved not to be the case, important qualitative differences were found among the samples tested. In particular, the addition of small amounts of stearic acid and alum caused major changes in the way the fibre surfaces were pyrolyzed. The chromatogram of pure cellulose pyrolyzed at 650°C was simple, as all of the decomposition products eluted near the front of the chromatographic profile (Figure 2A). Figure 2B shows the greatly changed pyrogram of paper to which both alum and stearic had been added, but which had never been aged. The new decomposition products in Figure 2B represented about 10% of the total weight of the cellulose, an order of magnitude greater than the amount of alum and stearic acid. These new decomposition products remained even after solvent extraction had left no stearic acid and only 200 parts per million of aluminum in the paper.

In research on cellulose containing a high concentration of carboxyl groups, Dahl [25], using thermal analysis, found that aluminum itself contributes to the instability of cellulose. He suggested that aluminum soaps are fixed onto cellulose by reaction with carboxyl groups on the surface. The adsorption of aluminum onto fibre surfaces is well known [12,13], and is essential, for example, in the proper use of dispersed rosin size. The fibre surfaces are sufficiently modified by aluminum and/or aluminum stearate coverage to

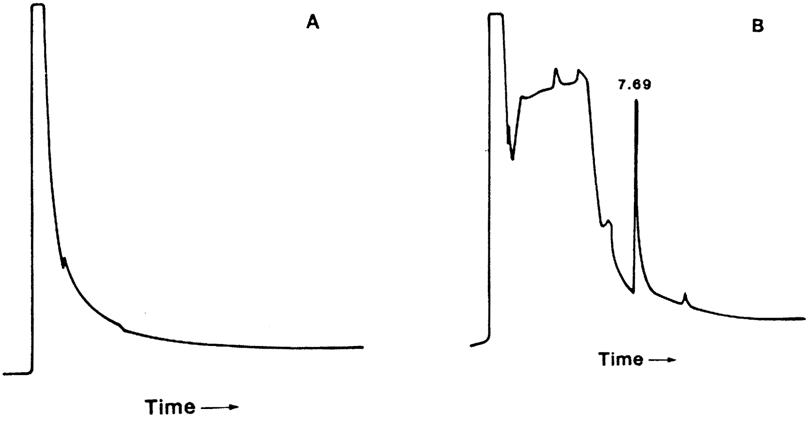

Fig 2—Pyrolysis-GC of paper samples. The peak at 7.69 minutes in B is stearic acid
A - pure cellulose paper
B - pure cellulose paper with physisorbed stearic acid and alum

change the mechanism of pyrolysis even after all or most of the stearic acid has been extracted, especially since only about a third of the aluminum is extracted with the stearic acid (Table 3).

It is well known that aluminum-fatty acid esters form polymers in aqueous media. In fact, pure aluminum triesters are impossible to prepare in anything other than totally anhydrous media [20] because of ready hydrolysis and polymerization. Thus, conditions which could lead to reaction between aluminum-based sizes and cellulose are also those which lead to extensive hydrolysis and polymerization. On the other hand, the synthesis of aluminum-fatty acid esters is a simple process. Industrially, this is done by heating aluminum oxide with fatty acid [21] (a reversible process [22]), or by precipitation of the sodium salt with alum [20,26] or aluminum chloride [27], so the room temperature formation of aluminum stearate by simple addition of alum to a paper containing fatty acid is quite possible.

The proposed [24] direct reaction between an aluminum ester and a hydroxyl group on a cellulose molecule is unlikely, considering the known instability of aluminum alcoholates in aqueous media [20]. However, mixed aluminum esters between cellulosic and fatty acid carboxyls are at least conceivable. Pure cotton cellulose contains about 8 milliequivalents of carboxyl groups per kilogram [28]. This corresponds to sufficient carboxyl groups to account for the nonextractable material by formation of an ester -- perhaps a mixed cellulose-aluminum-fatty acid ester. This ester bond would have been broken up by sodium methoxide treatment where solvent extraction had failed, and thus explains the recovery of stearic acid by sodium methoxide.

These results may explain the known difficulty in sizing high purity cellulose pulps, which contain a low concentration of carboxyl groups and other impurities able to coordinate with aluminum. It is also known that excessive amounts of certain organic acids -- particularly low molecular weight acids capable of strongly coordinating with aluminum -- will reduce sizing, perhaps by competing with coordinating groups fixed to the fibre surface. The synthesis of model compounds, starting with aluminum esters of glucuronic acid and its mixed esters with stearic acid would help to clarify the possibilities. Since the concentration of acidic groups in cellulose can be conveniently determined by conductometric titration [29], well-characterized fibres could also be used as experimental substrates.

The previous suggestion [16] that alum accelerates self-sizing in the same way that it accelerates conventional sizing has been demonstrated in these experiments. Just as a conventional size precipitate will adsorb onto a fibre surface, and spread in the drying process, so will alum added to a paper at the wet end or the finished sheet react with the natural resin and fatty acid material to produce complexes including free fatty acid and aluminum esters. They are produced even under low temperature drying of the alum solutions on the sheet, and develop more extensively with aging. While it seems unlikely that chemical bonds can form between hydroxyl groups on the cellulose chain and aluminum-fatty acid esters, further work should show whether the assumption is correct that esters can chemically bond to carboxyl or other acidic groups on the fibre surfaces.

In the introduction, we described some of the areas in which the surface chemistry of paper and of materials applied to it are becoming more complex. On the one hand, the prevention of self-sizing is important in areas where water-repellency is harmful, such as in the use of aqueous adhesives. On the other hand, alum-accelerated self-sizing is useful not only in understanding conventional rosin-alum sizing, but also as a potential low cost method of sizing materials containing natural resin and fatty acids.

APPENDIX I

Dynamic Surface Tension of Offset Fountain Solutions and the Surface Chemistry of Paper

Recent work [8,16,30,31] has revealed the importance of the time scale of measuring the wettability of paper. However, it is important to consider the time scale of the measurement not just from the point of view of the paper, but also from the point of view of the test liquid. A liquid jet subjected to a periodic disturbance will break up into regularly spaced drops. Information from the frequency and amplitude dependence of the jet breakup can give information on the dynamic surface tension of the fluid -- that is, the surface tension on the scale of a millisecond, rather than many seconds.

Examination of offset fountain solutions [23] has shown that at a one millisecond surface age -- the age at which new liquid surfaces come into contact with paper in the offset press -- the dynamic surface tension can be very different from the conventionally measured equilibrium value. At very short times, water-based fountain solutions show dynamic surface tensions close to that of pure water, no matter how low their equilibrium surface tension. On the other hand, fountain solutions based on aqueous isopropanol and on 2-ethyl-1,3- hexanediol show low dynamic surface tensions much closer to their equilibrium values. This finding helps to explain why fountain solutions based on alcohols are needed for less absorbent materials, such as coated papers.

Fluids with different dynamic and equilibrium surface tensions also had different sorption curves when used as test fluid on our dynamic sorption apparatus [30,31]. This observation suggested a method for determining the critical surface free energy of a paper. Fluids with dynamic surface tensions below the critical surface free energy of the paper will not show a wetting delay, while fluids with a dynamic surface tension above that of the paper will show a wetting delay. This concept is illustrated in Figure 3, while typical results are given in Table 6. Reasonable agreement is seen between the proposed method and values obtained by other techniques.

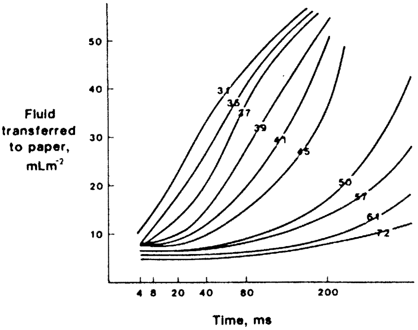

Fig 3—Gradual disappearance of wetting delay on self-sized newsprint in dynamic sorption curve with decreasing dynamic surface tension of test liquid. The surface free energy of the newsprint is taken to be equal to the surface tension of the test fluid (the numbers on the lines) for which the wetting delay (horizontal portion of the sorption curve) disappears. This occurs between 35 and 37 mN m^{-1}.

SAMPLE	MEASURED BY THE WETTING DELAY TECHNIQUE	INDEPENDENT MEASUREMENT
Sized paper	24	24
Fluorocarbon-treated paper	19	16
Reactive silane-treated paper	27	30
Fresh newsprint	39	37 - 41
Slightly self-sized newsprint	36	Not Available
Severely self-sized newsprint	30	Not Available

Table 6. Critical Surface Free Energies of Various Papers, mN m^{-1}

APPENDIX II

Techniques Used for Quantitative Analysis

Soxhlet extraction was carried out for 36 hours. The volume of solvent was reduced in a rotary vacuum evaporator. For gravimetric analysis, the last of the solvent was removed by room temperature drying in lightweight dishes. For gas chromatographic analysis the last of the solvent was removed by freeze drying. Aluminum contents of paper samples were determined by atomic absorption spectroscopy after wet ashing in a mixture of nitric and perchloric acids.

Extracts from the paper samples were examined quantitatively by capillary gas chromatography. Extracts of stearic acid in a 9:1 ether/methanol solution were methylated with diazomethane. Solvent and excess diazomethane were evaporated by a gentle flow of nitrogen gas bubbled through the solution. The internal standard was n-heptadecanoic acid.

Samples containing Triton X-100 were silylated in pyridine by reaction with a commercial reagent, Tri-Sil (Pierce Chemical Company). This is a 3:3:2 mixture of trimethylsilylimidazole; N,O-bis-(trimethylsilyl)acetamide; and trimethylchlorosilane. Cholesterol was the internal standard. Triton X-100 shows a broad distribution of peaks in its chromatogram, corresponding to components of different molecular weight. The Triton X-100 content was therefore determined by measuring the ratio of the area of the cholesterol peak to that of the nearest Triton peak and comparing this ratio to that for the injection of a known amount of Triton. Samples containing both stearic acid and Triton X-100 were only silylated. The omission of methylation did not affect the accuracy of the stearic acid determination, as long as the n-heptadecanoic acid internal standard was present.

Stearic acid (or its derivatives) that could not be solvent extracted even under exhaustive conditions (acetone followed by $CHCl_3$ followed by the benzene/ethanol 2:1 azeotrope) were debonded from the paper by boiling paper samples in a 0.02 M solution of sodium methoxide in methanol for 3 minutes. A known weight of n-heptadecanoic acid was used as internal standard. Unreacted sodium methoxide was destroyed by adding an excess of formic acid, and the amount of stearic acid debonded from the sample was determined by GC, as methyl stearate.

ACKNOWLEDGEMENTS

The authors wish to thank the Natural Sciences and Engineering Research Council of Canada for partial support of this work through an Undergraduate Research Fellowship to N. Chauret. D. Filion assisted in the GC analysis of extractives. Dr. Philip Whiting of Abitibi-Price Research Centre, Mississauga, Ontario, is thanked for his assistance in pyrolysis GC measurements, and Sylvie Sauriol for skilled technical assistance.

REFERENCES

1. Touchette, R.V. and Jenness, L.C., Tappi, 1960, 43(5), 484.

2. Grant, R.L., Paper Technology, 1962, 3(6), 539.

3. Christensen, P.K., Norsk Skogindustri, 1969, 23(10), 267.

4. Swanson, J.W., Tappi Engineering Conference Preprints, 1974, 327.

5. Nicolaysen, V.B. and Borgin, K., Norsk Skogindustri, 1954, 8 260.

6. McCallum, D.J.M. and Clifford, A.R., British patent 2 017 184, October 3, 1979.

7. Field, J.H., Tappi, 1982, 65(7), 93.

8. Aspler, J.S. and Lyne, M.B., Tappi, 1984, 67(10), 96.

9. Swanson, R.E., Tappi, 1978, 61(7), 77.

10. Takeyama, S. and Gray, D.G., Cellulose Chem. Technol., 1982, 16, 133.

11. Swanson, J.W., and Cordingly, S., Tappi, 1959, 42, 812.

12. Strazdins, E., Tappi 1972, 55(12), 1691; 1977, 60(10), 102; 1981, 64(1), 31; 1984, 64(4), 110.

13. Arnson, T.A., Tappi 1982, 65(3), 125.

14. Swanson, J.W., "Internal Sizing of Paper and Paperboard", TAPPI Monograph Series No.33 (1971).

15. Vandenberg, E.J. and Spurlin, H.M., Tappi, 1967, 50(5), 209.

16. Aspler, J.S., Davis, S., and Lyne, M.B., Tappi, 1984, 67(9), 128.

17. Collins, T.T., and Mulyk, J., Paper Trade Journal, 1980, (March 15), 25.

18. Swanson, J.W., personal communication.

19. Soteland, N., Norsk Skogindustri, 1976, 10, 364.

20. Leger, A.E., Haines, R.L., Hubley, C.E., Hyde, J.C. and Sheffer, H., Can. J. Chem., 1957, 35, 799-816.

21. Lower, E.S., Pigment and Resin Technology, 1982, 11 (2), 13-18.

22. Gordon, J.M. and Berger, R.S., Applied Spectroscopy, 1967, 21 (2), 65-70.

23. Aspler, J.S., Davis, S., and Lyne, M.B., Manuscript in preparation.

24. Gess, J.M., 1982 Papermakers' Conference Proceedings, Tappi Press, Atlanta, p. 9.

25. Dahl, S., Natl. Bur. Stds. (USA), 1970, Report No. 10-54.

26. Back, E. and Steenberg, B., Svensk Papperstid., 1951, 54 (15), 510-515.

27. Sheffer, H., Can. J. Res., 1948, 26B, 481-498.

28. Scallan, A.M. and Grignon, J., Svensk Papperstid., 1979, 82(2), 40.

29. Katz, S., Beatson, R., and Scallan, A.M., Svensk Papperstid., 1984, 87 (6), R53.

30. Bristow, J.A., Svensk Papperstid., 1967, 70(19), 623.

31. Lyne, M.B., and Aspler, J.S., Tappi, 1982, 65(12), 98.

Transcription of Discussion

SESSION 6 SIZING AND PITCH

Chairman **N.K. Bridge**

Mechanism of Self Sizing of Paper

by J.S. Aspler, N. Chauret and M.B. Lyne

Dr. D. Abson Weyerhauser Techn. Centre, Tacoma, U.S.A.

Not all self sizing involves resin or fatty acids. A good example of this is bleached Kraft pulp Douglas Fir which shows a considerable loss of absorbancy on oven ageing because of residual resins that are trapped in the parenchyma cells. However, these resins are entirely from the neutral steroidal fraction of the original wood extractives. The fatty and resin acids are removed in the original pulping operation. Now, in this case, the mechanism appears to be simply a melting and flow of the resins from the inside of the ray cells to adjacent fibre surfaces when the pulp is heated at 105°C.

Dr. J.S. Aspler This effect has also been seen in lower temperature work such as that by Swanson at IPC. We had to accelerate the process somehow.

Abson With Douglas Fir pulp, this phenomenon does not seem to occur to any great extent, regardless of time at normal storage temperatures.

Aspler There is certainly an effect of species; in Eastern Canada, there is much more self sizing where much pine is used, whereas in Western Canada, species such as hemlock seem to self size to a much lesser extent.

Abson One thing that influences the amount of residual resin after Kraft pulping seems to be the size of the pits in the parenchyma cells.

Aspler We have found it to be simpler than that. The species that self size the least appear to have the least extractive material.

Abson In any case, the accelerated ageing test appears to give misleading results as far as the tendency to self size, certainly in the case of Douglas Fir pulp.

Aspler We have monitored newsprints over 2 - 3 years storage and it would appear that two years storage in this way is equivalent to one day in the oven in terms of self sizing.

Abson In your paper, are you not describing a mechanism of oven ageing rather than a mechanism of self sizing in the accepted sense of a gradual absorbancy loss over a period of time at normal storage temperature?

Aspler The part that you describe was worked on in 1977 by Swanson and 1981 by Gray.

Abson I am referring to ester bond formation with fatty acids. Does this occur under normal self sizing conditions or is it just due to heating the pulp to 105°C?

Aspler I cannot answer that.

Prof R.H. Atalla IPC, Appleton, U.S.A.

The mechanism assumes that all the material which is not extractable, is chemically bound. At 24 hrs at 105°C, you can have crystallisation and aggregation in the structure, which could result in physical trapping of some of the components. This will also reduce the absorbancy because of the reduction in surface area. This can also be significant in mill operations when sometimes reels are stored for weeks. Workers at IPC have measured internal temperatures of reels and have found temperatures of up to 180°F 2 or 3 weeks after the reels have been made. So it seems to me that you have neglected the role of crystallisation and its consequences.

Aspler If you take high purity cellulose and put it into the oven for a week, there will be no loss in absorbancy. Is that what you are referring to?

Atalla High purity cellulose will not give you the comparison you want because typically, the purification processes or steps will result in almost complete crystallisation. However a pulp, especially never dried, has not aggregated to anywhere near the level of a high purity cellulose, e.g. cotton. A cotton pulp in its purification will have achieved as much crystallisation as in an oven at 105°C for 24 hrs.

Aspler I can only refer to the work we did on newsprint where we observed large differences between different samples. This can be attributed to differences in extractive content or differences in alum content.

Atalla I am not refuting what you are saying, I am suggesting another mechanism, namely, physical trapping of the resinous material as a result of crystallisation, may also contribute.

Aspler Yes, this may contribute because of the exposure to elevated temperatures over a period of time. Pulps which have not been exposed to elevated temperatures or refined after exposure to elevated temperatures, do change in crystallinity as a result of storage at 105°C for 24 hrs, or any exposure to elevated temperature at later stages.

Dr. R.W. Davison Hercules Research, Wilmington, U.S.A.

I believe that the exposed available surface area of the sheet that you were treating is much less than 1 m^2/g. What is your estimate for the exposed surface area?

Aspler The available surface area for paper is between 1 and 2 m^2/g. The lower figure being for pure cellulose, the higher for newsprint. Published figures that I have seen have always been between 1 and 2.

Davison When you give the filter paper your treatment, e.g. a brief application of alum, how long is that paper immersed in the solution?

Aspler About one minute. We tried the technique over various times, but the paper does saturate very rapidly.

Davison Do you feel that the exposed or available surface area of the paper might increase considerably during that brief immersion period or not? You estimate in your text that there are 4 monolayers of surfactant available on the surface. I would suggest it could be more like 10 - 20 layers based on my idea of the surface area of the filter paper, unless the paper opens up during the brief immersion to provide more exposed area for the surfactant to spread on. Also, in the 1950s, Bob Guide of IPC, proposed substituting resinate ions or groups along an olated hydroxy-aluminium polymer chain as the mechanism of rosin sizing. This could be an alternative explanation for your results.

Prof E.L. Back STFI, Stockholm, Sweden

If you continue to extract with a slightly acidic solution, e.g. hydrochloric acid containing a mixture of benzene and alcohol, would you then be able to completely extract all the resin material? This treatment would hydrolize all the partially bound resin material.

Aspler Yes I would expect this, as this is a standard method for determining rosin size. Under acidic conditions, all the material can hydrolise and be removed, but we have not checked this.