EFFECTS OF SIZING, ADHESIVES AND FILLERS ON THE FORMATION AND CONSOLIDATION OF PAPER WEBS

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Synopsis—The effect of additives of industrial importance in modern high speed papermaking is reviewed. These sizes, adhesives and fillers will be detrimental to formation, consolidation, physical and optical properties of paper or board, if they exist in a tightly aggregated condition and are poorly distributed in the fibrous product. Data are presented to illustrate suitable dimensions of the solid particles to supply the desired property with the least amount of addition. The retention of the additives without sacrifice of their efficiency is a difficult problem.

Alumina precipitates can decrease paper strength to very low values, but can increase it again with additional aluminium sulphate. The absence of sulphate ions permits gain in strength above the starting value. Anionic polyacrylamide, carboxymethyl starch, urea-formaldehyde and cationic melamine-formaldehyde resins become considerably more effective with a closely controlled alumina compound. Recent studies on the degree of neutralisation of alum and the advantage of a moderate cationic charge in rosin sizing are reviewed, as well as an explanation for the improved efficiency of fortified rosin and synthetic sizes. Bridging by polyacrylamide molecules, the sorption and movement to fibre contact areas by molecules and macromolecular fragments from cationic starch are discussed.

Evidence is presented for the agglomerated state of pigments in paper and electron micrographs establish that titanium dioxide can be retained at about 0.25 μ. Modern criteria for pigment evaluation are given. Debonding reduces pick resistance in offset printings, but helps in the ability to run letterpress paper.

Alumina compounds

THE most widely used additive in papermaking is aluminium sulphate and the few exceptions are easier to list than the numerous applications. Well known is sizing at above pH 7.0 with alkyl ketene dimer, when the amount of aluminium sulphate must be held to a minimum. Another exclusion applies to highly absorbent papers, for which self-sizing must be

avoided. Therefore, aluminium sulphate is omitted and the pH value adjustment for the curing of wet strength resins is made with hydrochloric acid. Most other papers or boards receive at least residual aluminium sulphate from the purification of fresh water or the addition was specified by operators to reduce a sticking of the wet web to guide roll or wet press rolls. Aluminium sulphate is widely used to improve the retention of fibre fines, fillers, wet end adhesives and rosin sizing.

The publication by Barrow[1] re-emphasised the harmful effects of acidity upon the permanence of paper to be stored for long periods. Papers with a cold water extract below pH 6.5 lost folding strength and became brittle with natural ageing or oven ageing. Data by McCann (Table 1)[2] on handsheets made from refined strong unbleached pine kraft pulp with mill water show a decrease in several strength properties. The burst factor dropped from 57 to 14 and the MIT folding strength from 840 to 12 at the fairly high

TABLE 1—EFFECT OF ALUMINIUM SULPHATE ON ALL UNBLEACHED PINE KRAFT
(530 CSF)

	Tear factor	Burst factor	Breaking length, m	Stretch, per cent	MIT fold	Density
No addition	127	56.7	8097	3.4	839	1.69
2 per cent alum and sulphuric acid to pH 5.5	130	47.6	7225	2.7	452	1.76
Alum to pH 5.5	204	13.9	3340	1.5	12	1.83

Data by McCann[2]

value of pH 5.5 when alum was used exclusively. The strength losses were still substantial with 2 per cent alum and sulphuric acid. Keller[3] and Prusas[4] made a similar study on a typical mixture of refined bleached pine kraft and bleached hardwood kraft again with water containing calcium or sodium bicarbonate. Fig. 1 shows the not unexpected decrease in strength properties such as MIT folding strength (plotted as the logarithm of fold) upon addition of aluminium sulphate. It is noteworthy that the folding strength could be raised again with the next increments of alum. Other tests confirmed this decrease in strength to a minimum, which was followed by a gain in strength with additional aluminium sulphate. The burst factor started at 45 lb/in² dropped to 5.6 lb/in² and increased again to 38 lb/in². The original breaking length of 5 930 m was reduced to 1 520 m, then more alum brought it back to 5 610 m. Fig. 1 illustrates the increase in ash content from 0.43 per cent to 10.2 per cent, followed by a reduction to 3.65 per cent. Chemical analysis showed that the retention of calcium salts in the paper was very low. The curve for

pH value is given in Fig. 1, together with the changes in the scattering co-efficient (100S), which started for the paper at 3.04, increased to 4.52, ran parallel to the content on ash content and dropped to 2.76. Data for caliper, the bulk of the sheet (cm^3/g), Gurley porosity, Taber stiffness, smoothness and brightness are available. Careful moisture tests on conditioned samples showed a change from 7.2 per cent to 9.68 per cent back to 8.03 per cent. A second study confirmed these observations.

The exclusive use of distilled water in place of mill water did not cause an increase in ash content of these sheets. Neither was the decrease in breaking length from 6 640 m to 6 170 m as dramatic as in the cases with mill water.

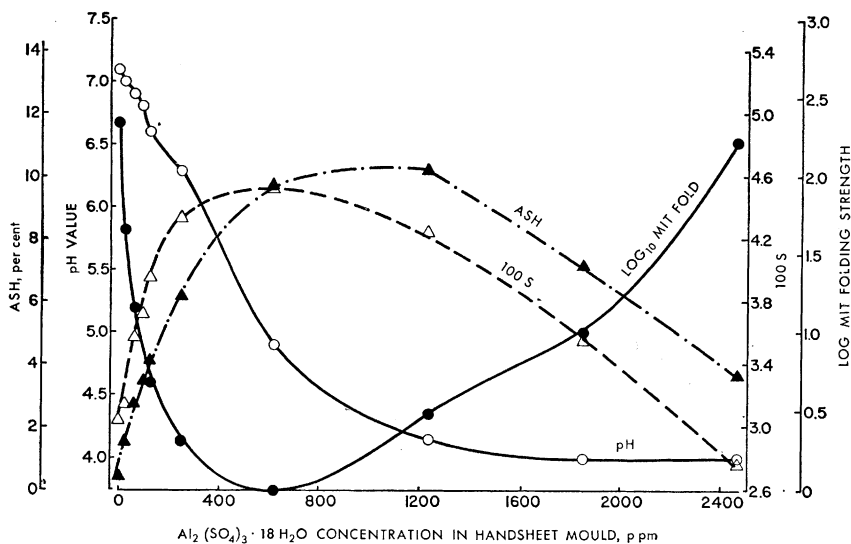The investigations by Lagally[5] demonstrate that such losses of strength

Fig. 1—Effect of alum added to hard water on various pulp properties, furnish A

can be reversed into gains of strength above the original values for the pure pulps: 5–10 per cent of the reaction product from sodium aluminate and aluminium chloride were added in handsheets made from lightly processed papermaking pulps (bleached kraft or hardwood soda or sulphite). Re-circulated whitewater was used. The bursting strength was increased from 30.7 to 40 and folding strength from 110 to 272. Lagally reports in another experiment an increase in Mullen bursting strength from 17.0 to 23 lb/in^2 for a constant TAPPI opacity of 80 by changing from 3 per cent alum to 3.7 per cent alumina free of sulphate ions. The obvious conclusion is that alumina compounds can increase or lower strength.

TABLE 2—EFFECT OF ALUM ON MIXTURE OF BLEACHED PINE AND HARDWOOD KRAFTS

$Al_2(SO_4)_3 \cdot 18H_2O$, ppm	Head box pH value	Ash content, per cent	Bulk, cm³/g	Burst factor	Tear factor	Breaking length, m	MIT fold	Gurley porosity sec	100S	Taber stiffness	Sheet moisture content, per cent
0	7.1	0.43	1.65	45.2	112	5930	216	18.3	3.04	1.30	7.20
100	6.8	3.41	1.65	15.8	127	3240	9	21.1	3.72	1.24	7.95
200	6.6	4.09	1.70	12.5	129	2890	5	23.1	3.95	1.23	8.27
300	6.3	6.40	1.67	8.0	115	2090	2	25.0	4.32	1.14	8.56
600	4.9	9.67	1.68	5.6	81	1520	1	28.8	4.52	1.08	9.56
800	4.5	10.18	1.63	8.8	—	2080	3	43	4.35	—	9.68
1600	4.0	7.1	1.60	15.0	—	3300	40	40.9	3.54	—	8.95
2400	4.0	3.65	1.62	38.0	111	5610	161	30.6	2.76	1.32	8.03

Data by Prusas[4]

Reynolds & Linke[6] show that at a low pH value (below about 4.2) the retention of alumina and sulphate is very low. Their handsheets were made with deionised water from Northern coniferous kraft pulp. This observation helps to explain the reduction in ash content in the tests made by Prusas when more alum was added.

In a parallel study by Prusas with a different mixture of the identical pulps, a nearly constant ash content was obtained from 60 ppm alum and from 2 500 ppm alum (4.69 per cent against 4.41 per cent ash). The pH value at the lower alum concentration was 6.7. The burst factor had dropped from 41 for pulp without alum to a value of 11.2. Upon addition of excess alum to give pH 4.0, the burst factor at 4.41 per cent ash content was increased to 30.

The lower strength at the higher pH value is not caused by a higher ash content, but either by a greater retention of sulphate ions in the paper or by a different alumina complex. Reynolds & Linke[6] stress that the composition of the precipitate retained within the paper will vary with the pH value at which the sheet was made. The drying of the paper will release free hydrogen ions. Drying at a higher temperature converts more aluminium to the insoluble oxo-form and more severe heating increases the proportion of free hydrogen ions. Thomas[7] adopted Werner's studies of aluminium complexes and Cobb & Lowe[8] added evidence to support the co-ordinate role of alum. Matijević[9] finds his data to be consistent with the Thomas postulate of olated aluminium polynuclear ions. He proposes the formula of $Al_8(OH)_{20}^{++++}$ for the complex aluminium ion. Matijević[10] states that recent studies with aluminium sulphate confirm his previous results with aluminium nitrate so long as the sulphate concentration is low. The increase in strength reported by Lagally 'may be due to a complex ion'.

The available papermill data on the effect of aluminium sulphate in grades for which the preservation of the original strength or its improvement are very important are not so well documented as the studies by Prusas or Lagally. Watkins[12] has emphasised that the composition of the water and the reaction conditions for aluminium sulphate, not only its amount deserve much more attention. A critical analysis of stickiness on couch or press rolls will lead to a more efficient solution than the present one with alum. The application of research in coagulation problems has already shown that alumina may be replaced by newer retention aids, by which a loss in strength can be avoided. Basic aluminium chloride[13] may replace alum, if it becomes competitive in price with the very economical aluminium sulphate.

Resin and synthetic sizing

Examples of loss of strength—Linke[11] shows a loss of bursting strength of 7 per cent by 1.0 per cent of rosin and of 26 per cent by 2.5 per cent rosin

compared with paper made with the identical amount of aluminium sulphate, but without rosin. Such reduction in the burst factor from 86 with alum to 63 with rosin and alum will prevent acceptance, if this product has to meet specifications for packages. Watkins[12] shows losses of 20 per cent in bursting strength for an addition of 0.75 per cent fortified rosin size at pH 4.5 for paper made entirely from high white pine kraft pulp. A pine kraft pulp of 85 per cent brightness lost 17 per cent on bursting strength with 1.5 per cent rosin at pH 4.5. Pine kraft pulp of 70 per cent brightness at 500 CSF lost 8 per cent bursting strength and, at 200 CSF, the reduction was 7 per cent. This low loss should be contrasted with the 35 per cent reduction in the case of a mixture of 60 per cent high white pine kraft and 40 per cent hardwood kraft pulps.

Sanyer's data[14] show that a reduction in rosin size from the large amounts described above to very low additions is promising, if the degree of sizing will be sufficient. The burst factor of unbleached pine kraft pulp at 350 CSF dropped by 10 per cent if 0.3 per cent rosin, 0.4 per cent alum and sulphuric acid to pH 4.5 were applied. No loss in strength occurred when synthetic size was furnished in place of rosin/alum. The supplier of both sizes lists in a bulletin[15] a burst loss of 21 per cent for rosin size at pH 4.5 compared with ketene dimer* at pH 7.5, if the tearing strength was specified as 200 g. At a tearing strength of 150 g, rosin size decreased the bursting strength by 24 per cent. Barber[16] had demonstrated the important relationship of bursting and tearing strengths.

The preservation of high brightness is very important to meet specifications in white papers that approach the reflectivity of the brightness standard. Paper without any additions and aged for 48 h at 105°C lost 5.3 points in brightness; paper with 1 per cent fortified rosin size and 2.5 per cent iron-free alum started 2.3 points lower and dropped 6.6 units when similarly aged; 2 per cent fortified rosin with 2.5 per cent alum was 7 points lower on ageing than paper without additives, whereas sheets with ketene dimer sizing matched the latter. A decrease in the amount of rosin size minimises the foaminess of the head box stock. Foam generally harms formation and defoamers can decrease paper strength, even if they overcome the formation deficiency.

Threshold demand on ketene dimer—A reduction in the amount of size without sacrifice in the required resistance to liquids, is a valuable contribution to better formation and consolidation. Swanson[17] demonstrated that minute quantities of stearic acid are sufficient for 'ample sizing against water'.

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* This and later mentions of ketene dimer refer to Aquapel

The smallest amount of sizing material under commercial papermill conditions was observed by Kincannon[20] for an unbleached softwood kraft sheet. A very high Hercules ink photometer test of more than 4 500 sec was obtained with 0.008 per cent of ketene dimer or the alkyl ketene dimer of palmitic and stearic acids. This percentage is the quantity that reacted with the free hydroxyls of the cellulose fibres to form an ester. It was necessary to add at the papermachine head box 0.015 per cent—or 150 g (dry basis)—for 1 000 kg dry fibre, since a retention of 65–85 per cent is typical. Approximately 65 per cent of the retained quantity will react with the fibres, 35 per cent being lost by hydrolysis upon reaction with the water in the wet sheet, since a ketone of low sizing value is formed. A much higher drying temperature at the beginning of the dryer section improves the reaction of the synthetic size with the hydroxyls of the cellulose. This explains why ketene dimer is very effective on Yankee machines with higher drying temperatures.

A bleached kraft paper of 40 lb substance was sized to an ink photometer test of 850 sec with 0.037 per cent reacted ketene dimer. Bleached meat wrap of 42 lb substance with a resistance against liver blood for 24 h is being sized with an addition of 0.15–0.20 per cent ketene dimer and of 0.1 per cent of a polyamide amine epichlorohydrin as a retention aid and wet strength resin. Not only is this paper stronger, but the expense for sizing is cut to one half. In the previous procedure, a meat wrap required 1.75 per cent fortified rosin size, 0.25 per cent paraffin wax size, 0.5 per cent cationic urea-formaldehyde wet strength resin and 2 per cent aluminium sulphate.

The improvement in strength and brightness by the elimination of rosin and alum is particularly important for airmail stationery of very low substance or for permanent papers made from pure cotton fibre or high alpha-cellulose pulps. These papers are very difficult to size without excessive amounts of special rosin sizes.

Davis[21] found that ketene dimer dissolved in a solvent produced very hard sizing with 60 per cent less dimer than necessary with an emulsion. This is a very good confirmation of Swanson's extremely low value of 0.006 per cent stearic acid, which he found necessary for good sizing. Sizing dry paper with modern economical solvents is not unlikely in the future. Currently, the spraying of the formed web might be next in efficiency, but the occasional malfunctioning of the sprays a few years ago led to the development of ketene dimer emulsions for internal addition. Emulsions usually reduce paper strength, but the application of cationic starch as protective colloid and cationic wet strength resin as retention aid compensated for this decreased efficiency. In papers of light substance, retention of ketene dimer is obtained by depositing it on a silica filler. This introduces new problems because of the very low 'single pass retention' of fillers on high speed papermachines.

Therefore, it is preferred to bring the emulsion particle by a cationic charge close to the fibre, similarly to cationic wet end starch or cationic wet strength resins. The emulsion particle with highly swollen cationic starch is rather large at 1–2 μ 'to help retention'.

It is not understood why the separate addition of 0.01–0.1 per cent cationic polyamide amine epichlorohydrin immediately before forming the web improves the retention of cationic ketene dimer. Therefore, it is not surprising that several modifications of these resins must be evaluated by trials rather than by measurement of well-defined properties. In the case of milk bottle board, Kincannon[20] found that it had to be formed with smaller capillaries than with the previous rosin sizing. This was vital to retain the 0.2 per cent ketene dimer and to obtain resistance for 24 h against lactic acid. Retention of cationic ketene dimer is facilitated by anionic mannogalactan and calcium carbonate filler. Kincannon[23] shows that a fivefold higher ink photometer test value is obtained by control of the alkalinity of the water to 150 ppm (expressed as $CaCO_3$), because of a better reaction of ketene dimer with the cellulose, which was refined in the presence of sodium carbonate.

The varying response to sizing by different pulps is well known. Unbleached kraft pulp is the easiest to size with rosin size or ketene dimer; next are bleached kraft and bleached sulphite pulps. The high ink resistance of cotton linters with 0.12 per cent dimer is noteworthy compared with the 2 per cent rosin size. The test figure of 19 sec for rosin size against 909 sec for the synthetic size shows up well the different reaction mechanism of the two sizes.

The small amounts of ketene dimer emulsion must be added with care to a highly dilute stock suspension to obtain excellent distribution. Violent agitation must be avoided. The cationic charge on the ketene dimer particles facilitates their approach to the fibres, which carry patches of varying anionic intensity. These attachments are not strong enough to withstand the action of centrifugal cleaners at the papermachine. The ketene dimer (as for other valuable additives) should not be wasted by introducing it into the whitewater, where debris with large surface areas will use up an amount out of proportion to any possible benefit.

The hexadecyl ketene of molecular weight 530 is distributed apparently as molecules upon the cellulose fibre surface and forms a β-keto ester with the hydroxyl groups of the cellulose. Some migration takes place during several days of ageing after the paper has left the papermachine. The electron micrographs (Fig. 2) show untreated cellulose and cellulose treated with ketene dimer, whose molecules are not visible, owing to their small size, whereas several electron micrographs of rosin-sized fibres show particles as discussed below. Most of these comments for alkyl ketene dimer are applicable in general to other synthetic sizes.[25]
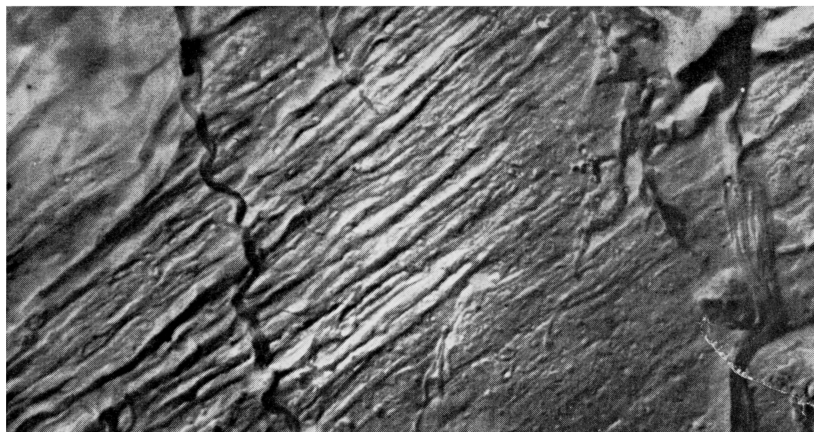
***Fig. 2***—Ketene dimer particles on cellulose [× 11 750]

Fortified rosin size—Modern fortified rosin sizes have replaced the old type of rosin size widely, except for the deep brown, low cost papers, which can be sized with the dark wood rosins of B or F colour designation. A good illustration of wasteful usage of rosin size with paper is the observation[20] that 95 per cent of the rosin in paper could be removed by extraction. The remaining 5 per cent rosin produced better sizing than before the extraction, probably because of the more efficient alignment of the rosin precipitate. This better redistribution most likely was caused by sizing from a solvent solution.

Fortified rosin sizes were improved again during 1963. Surface-sized bond papers or unbleached liner board can be adequately sized with 0.3 per cent rosin. This remarkable reduction in amount of size used minimises the loss of paper strength, but has required great efforts. Closer control of gum, wood or tall oil rosin quality has helped. Tall oil rosin is now a very desirable source, since the formation of crystals (three molecules of abietic acid with one molecule of alkali abietate) has been overcome with formaldehyde. Floating of the size or foaming or high viscosity have been minimised. Disproportioning* of the rosin has raised brightness of paper from 70.7 per cent after ageing (loss of 11.2 points from the original brightness) to 75.3 per cent. The Diels-Alder reaction of a part of the rosin with maleic anhydride or fumaric acid does introduce two additional carboxyl groups and forms the fortifier for the size. Blechinger[30] mentions that alcohols are introduced

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* Transformation of a substance into two dissimilar compounds by a process involving simultaneous oxidation and reduction

to form esters with the anhydride groups. Therefore, a modern rosin size may contain methylol groups, adducts and esters.

These various changes have decreased the particle size. Electron micrographs supplied by Linke[26] show well-dispersed particles of fortified size of 150–300 Å diameter. The unfortified rosin size consists of coalesced particles of 500–2 600 Å. The two carboxyl groups are located on one end of the maleo-pimaric acid molecule formed in the Diels-Alder reaction. Disproportioning or heat treatment at 250°–310°C for 4–6 h changes the abietic acid into the dehydro-abietic acid that contains the one carboxyl at the
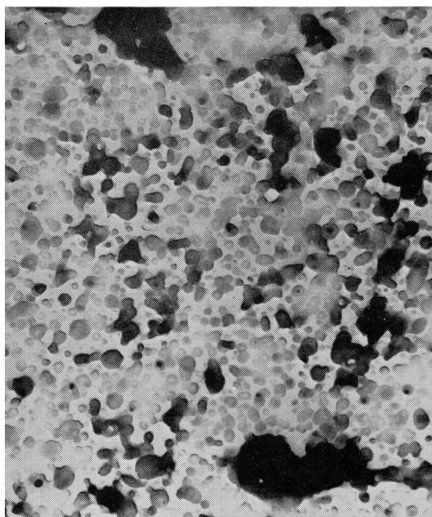
Source: American Cyanamid Co.

Fig. 3—Colloidal rosin size—not fortified, coalesced [× 10 000]
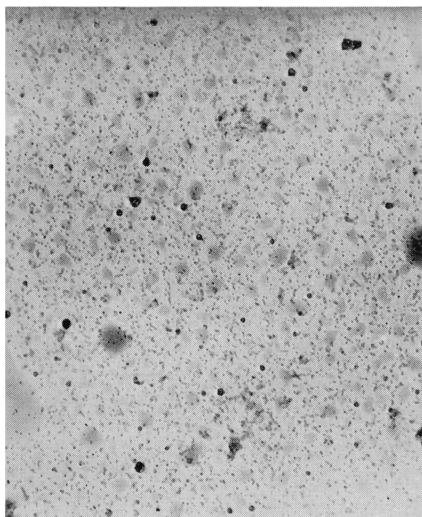
Source: American Cyanamid Co.

Fig. 4—Colloidal rosin size—fortified, well-dispersed [× 10 000]

opposite end of the molecule. Linke postulates and Strazdins[31] confirms that the surface area of a monomolecular film of fortified rosin is larger than for regular size. A better coverage of the fibre and good sizing can be expected, if the carboxyl groups are directed towards the fibre surface.

Langmuir,[27] Guide[28] and Watkins[29] have emphasised the importance of the orientation of the hydrocarbon end of the rosin molecule away from the fibre surface to obtain efficient sizing with a minimum amount of rosin. Occasionally, carboxyl groups are oriented outwards from the fibre.

Watkins[29] discusses this overturning of molecules and the resultant decreased sizing. Strazdins[31] observed size precipitates that carried a strong negative charge when a positively charged aluminium floc was expected. He

assumes that this negative charge stems from the adsorption of chemically unbound ionised rosin acids. The rather high retention of rosin in this case did not produce good sizing.

In the preparation of efficient ketene dimer emulsions, it is essential to provide the best emulsifier and protective colloid and to apply excellent mechanical dispersion. In free rosin sizes or free rosin dispersions (both with fortifiers), these factors are just as important. The forming of a primary emulsion, then of a secondary emulsion in the latest automatic rosin size emulsifiers is still much of an art. The dispersed size particles should not be prematurely aggregated, since not only the smaller number of aggregated rosin precipitate particles, but a random orientation of hydrophobic groups will reduce the sizing effect. Recycled whitewater or a reaction between rosin size and aluminium sulphate that is too rapid—Strazdins[31]—causes agglomeration of amorphous precipitates. An addition of alum first to the fibres, followed by rosin size which is introduced into dilute head box stock, has increased the degree of sizing considerably in selected cases.

TABLE 3—ELECTROPHORETIC MOBILITY OF PULPS
AT pH 4.5 WITH 100 ppm $Al_2(SO_4)_3 . 18 H_2O$

Pulp	*Mobility, sec/volt/cm*
Cotton linters	0.4
Bleached kraft	0.4
Unbleached kraft	0.75
Bleached sulphite	0.90
Unbleached sulphite	1.60

Data by Vandenberg & Spurlin[33]

Strazdins[31] specifies that the final net surface charge of the sized fibres must be relatively low, preferably on the positive side. Therefore, the amount of aluminium ion and its surface charge as measured by micro-electrophoresis —Black & Smith[32]—must be controlled and the moderation of the positive charge by sulphate ions (counterions in the double layer) must be appreciated.

The degree of the neutralisation of the three positive charges of aluminium ion by hydroxyl is important. Strazdins confirms Ekwall, Guide and others that sizing develops only with the more complex hydrated aluminium ions. The Matijević[9] formula $Al_8(OH)_{20}^{++++}$ is considered by Strazdins to be an important contribution.

Vandenberg & Spurlin[33] reviewing the mechanism of rosin sizing in their Emil Ott Memorial Lecture present microelectrophoretic mobility measurements for several pulps (Table 3). The negative charges are due to anion active water solubles, which in bleached sulphite pulp contain uronic

acid groups. Adsorbed hydroxyl and sulphate ions are present. The poly-uronides in the pulp or additions of citrus pectin, etc. reduce the charge of the size precipitate and its normal tendency to grow into coarse agglomerates. This results in the much desired better distribution of the size in the paper. Unbleached pulps might be easier to size because of a stronger interaction.

Strazdins[31] reports a very low retention of rosin when he applied at pH 4.8 a high concentration of highly cationic aluminium chloride. The mobility of the fibre with aluminium chloride was $+1.2$ and was raised upon addition of colloidal rosin to $+1.7$. This illustrates the situation in which excess cationic charge on the fibres obstructs the adsorption of the sizing complex. Strazdins agrees with Thode[34] that the reaction of rosin with aluminium ion already adsorbed on cellulose is usually the minor reaction. The major amount of the aluminium ions remains in the solution and reacts with the rosin size or rosin dispersion. 'The complex aluminium rosinate owing to its hydrophobic nature tends to escape from the water phase and adsorbs on the cellulose more readily than the complex aluminium ions.'

Strazdins concurs with Guide[28] that the retention of any beater additive can be explained by physical adsorption in which short range Van der Waals forces are operative. 'The electrostatic attraction is superimposed on the basic Van der Waals attraction.' Owing to their long range effectiveness, the electrostatic forces can convey cationic particles into the proximity of anionic surfaces. Under dynamic mill conditions, the retention may occur to some extent by a less desirable filtration process. The physical adsorption may be incomplete because of a limited contact time or insufficient movement to the fibre surface. A lack of mild agitation at high consistency is undesirable, but excess agitation is not wanted either, since it may rub off the adsorbed size precipitate from the fibres.

Arledter[35] and Jayme & Arledter[36] confirm that a smaller particle size improved the resistance against test liquids. The single pass or first time over the papermachine retention of a rosin dispersion with 77.3 per cent free rosin fluctuated badly from 37 to 68 per cent, whereas a rosin size with 37 per cent free rosin gave a yield of 62–73 per cent in the paper. A fully saponified size was retained well at 82–85 per cent. Arledter observed that the retention was proportional to the wet weight after centrifuging. He designed a test similar to Jayme's water retention value of beaten pulps (centrifuging under specified conditions). A size precipitate holds more water in proportion to its content of aluminium mono-, di- or tri-resinate; free rosin has no affinity for water. The aluminium resinate may contain four hydroxyl groups and some rosin acids co-ordinated with aluminium.[28]

No analysis seems to be available, if Brownian diffusion forces are in-volved in retention of rosin size, as has been shown for the capturing of

titanium dioxide by fibres in Johnson's work.[37] Size resistance can be increased by the addition of cationic urea formaldehyde, melamine-formaldehyde or polyamide amine epichlorohydrin resins. These materials improve the retention of fibre fines, which are rich in rosin precipitate. The fibre


Source: Nalco Chemical Co.

Fig. 5—Fortified rosin size and alum [× 20 340]

debris becomes less effective in repeated passes through the whitewater and saveall system, which occurs in the usual operation without such retention aids.

The efficient retention of rosin precipitate at optimum particle size will not provide satisfactory sizing, unless drying is well controlled. The evaporation of moisture on a vacuum dryer at 120°F prevents the sintering or change in shape and light transmission of the size precipitate. Therefore, little

sizing is developed. The writer[40] showed that contact of the paper against very hot surfaces at the end of the dryer section improved ink flotation 10- or 12-fold and gave the desired sharper and glossier writing ink (feather) lines. Studies by Arledter and by Kaltenbach[41] confirmed these observations and showed how size composition and precipitation conditions influence the
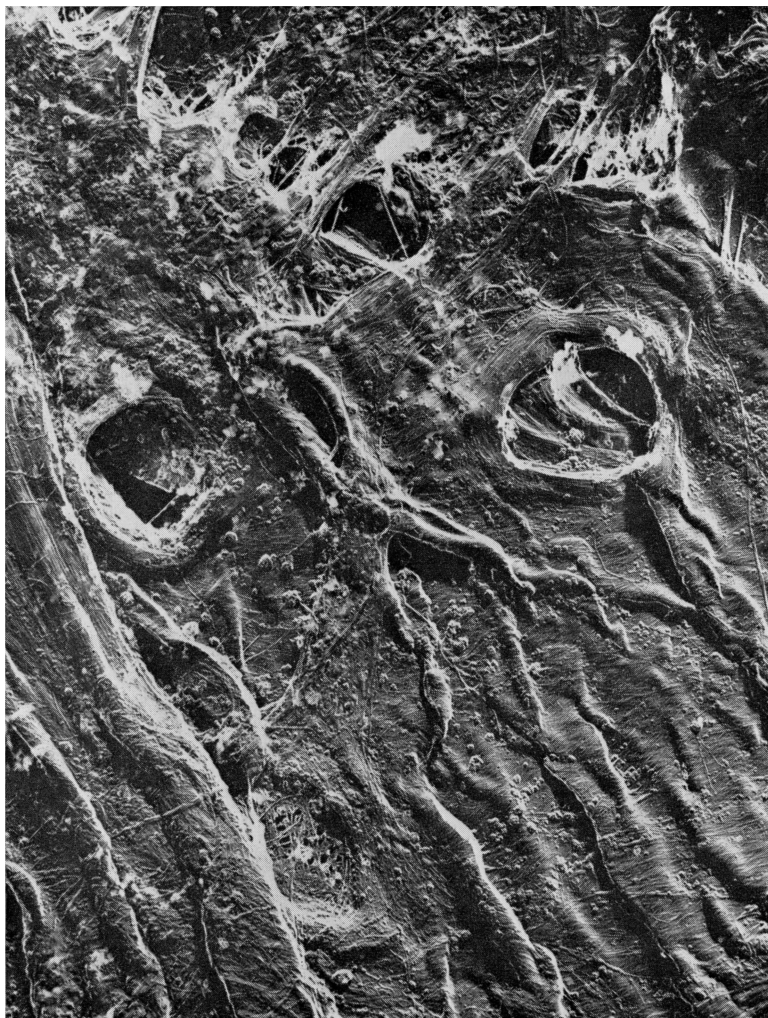
Source: Hercules Powder Co.

Fig. 6—Paper replica—2 per cent fortified rosin size and alum drum-dried [× 5 000]

sintering temperature. Davison[42] finds that the better mobility of the size precipitate during drying at higher temperature explains the improved sizing. 'Bound resinates are less mobile and should be avoided, since the dried deposit will be superior if it contains a certain amount of free rosin together with aluminium diresinate.' Brecht & Wenzel[43] added 25 per cent fortified size into the regular size. This overcame the migration of regular rosin size from the smooth to the rough side of MG paper on a very hot Yankee dryer. Davison[42] interprets electron microscope pictures to show individual particles of 1 000 Å in size. They may be arranged like a bunch of grapes. The electron microscope pictures by Kobayashi & Komagata[44] show size precipitate adhering to fine fibrils that are still connected to the fibre. No trace of rosin particles could be found on a smooth unfibrillated layer after removal of the primary and outer secondary wall. The pictures by Nelson[45] show particles of 300 Å and several clusters of 1 000 Å.

Sizing with fortified rosin sizes has been greatly improved, but even higher efficiency is possible if the random distribution and local excess is replaced by a more uniform distribution. Strength is lost by rosin precipitate clusters. Less size will be required if the wasting of rosin on fibre debris is prevented.

Sizing against writing ink at the size press—The Reichhold Company and others[46] have stated that, upon addition of a modified urea-formaldehyde resin to the starch in the size press, the rosin size in the base sheet could be reduced by 30–50 per cent. Equal sizing against writing ink was obtained. The cut in rosin size increases the drainage rate on the machine wire and permits better sheet formation. Faster drainage allows a greater stock dilution, which improves formation. Monsanto[47] finds that small amounts of the half ester of butyl alcohol with styrene maleic anhydride added to the starch solution increases sizing. Reinbold[18] reports that cationic mixed polymers based on acrylic acid esters are effective additions to the starch. A waterleaf sheet is led to the size press and offset papers of higher pick resistance are produced by an increase in the impregnation of the base sheet with starch. One trial paper contained 3.45 per cent starch and 0.5 per cent polymer. This increased the Dennison wax test on the top side from 11 to 15 and on the wire side from 15 to 19. The breaking length was raised from 2 500 m to 3 100 m.

Wet end adhesives

Objectives—The addition of wet end adhesives such as the various starches, mannogalactans, cellulosics, polyacrylamide, latices or wet strength resins must be justified by a critical analysis. The correct functional properties of the paper product and the adequate use of refining, wet pressing or drying facilities must be assessed before the incorporation of adhesives.

Barber & Ware[16] recommend examining the *power substitution value*—the saving in power feasible by reduced refining in relation to the advantages and cost of the adhesive.

Today, not only standard refining, but high consistency refining must be reviewed. An increase of 50 per cent in the bursting strength of kraft liner of 20 lb/1 000 ft^2 substance at 970 ft/min has been claimed for the replacement of table rolls with foils by Thorp,[48] probably because of the paper's greater uniformity, with fewer poorly bonded areas. The modern wet pressing with the fabric press or the grooved press needs examination. Wet paper should not be damaged by uneven release from couch or press rolls. Elimination of stickiness can be very important. Occasionally, low bursting strength can be overcome by a reduction in the paper draws during drying.

These steps do not increase fibre length and the fibre substitution value indicates if greater fibre length obtained by less refining will permit use of more economical short-fibred pulps. The *property disproportionation value* shows if an additive can increase bursting strength without an undesirable decrease in another important property such as air resistance, as happens in refining.

Polyacrylamide for dry strength—This anionic synthetic product is of great interest, since its application is increasing in spite of a 12-fold higher price than beater starch. Very small amounts such as 0.1 per cent do increase paper strength. The production can frequently be raised by 10–25 per cent through better drainage on the wire or easier drying. Reynolds[49] claims that the resin provides additional bonds between fibre surfaces when the distance is too great for hydrogen bonding. 'The resin can double the strength with very little change in density, porosity or light scattering.' Its efficient usage depends on a control of the cationic surface charge of aluminium sulphate after the best ratio of hydroxyl to aluminium ion has been established similar to the recent findings of Strazdins for rosin sizing.

Molecular weight and length of branches in natural adhesives can only be decreased. The research efforts of large chemical concerns proved that in synthetic polyacrylamide an increase in molecular weight from about 100 000 to 600 000 was beneficial. It raised bursting strength from 20 to 30 lb/in^2 and it doubled the MIT folding strength. The introduction of about 10 per cent carboxyl groups during the copolymerisation of acrylamide and acrylic acid produced a peak in tensile, bursting or folding strengths; smaller or higher contents of carboxyl groups gave lower strength. Linke[50] states, 'Too much carboxyl in the polymer molecule leads to a highly negative polymer, which requires far too much alum for retention and whose effective amide-hydrogen bonding groups are reduced in number.' Jones *et al.*[51] find that the repulsive effect of negative charges from the carboxyl groups

(produced in this case by hydrolysis of amide groups) at a pH value above 4.0 will extend the polymer chains. A bridging from one fibre surface towards another layer above or beneath the first layer might explain why polyacrylamide is particularly effective in increasing the plybond strength between the several plies of a food board made on a cylinder machine. Considerable increases in Dennison wax test results were observed, if high wet pressing was applied (wax pick from 10 to 16). In a bleached sulphite paper, a bursting strength of 33 lb/in² was obtained with 0.5 per cent polyacrylamide with very light refining, whereas severe processing was necessary without the additive. The freeness was reduced by extra refining from 470 cm³ (Green) to 110 cm³, with corresponding adverse changes in drainage and fibre length. Linke emphasises that dry bursting strength can be raised in increments with additional polyacrylamide up to 65 per cent above the value for untreated papers. For a mannogalactan, a plateau in strength gain was observed at 28 per cent. A modified starch levelled off at 22 per cent higher bursting strength. Linke explains these gains by a 'filling in between the fibrils and around the fibre-to-fibre contact points'.

Electron micrographs indicate that 'the resin exists as many small discrete particles'. Thus, Reynolds continues, 'it is postulated that the resin particle bridges between two or more fibres separated by distances too great for hydrogen bonding'. It appears that the concept of bridging is necessary to explain the continual gain in strength with more polyacrylamide. A mere crowding of adhesive near the fibre contact points will not raise strength beyond a certain level. This seems to be the case with other adhesives with which bridging by polymer chains is not to be expected.

The application of 1.5 per cent polyacrylamide for maximum strength with bleached kraft pulps is rather expensive at $18/ton, whereas the frequently realised increase in tonnage by 15 per cent with an addition of 0.2 per cent polyacrylamide is of real benefit. Linke demonstrated the importance of cationic alumina. Holding the amount of polyacrylamide constant, a 10 lb/in² bursting strength was realised with 1 per cent alum compared with 15 lb/in² with 3 per cent alum. The optimum pH value for highest strength was pH 4.2, when 6 per cent alum was present at a fibre consistency of 3 per cent. The same strength was obtained at pH 4.5 when 1.5 per cent alum was available in stock of 0.6 per cent consistency. Linke's graphs show narrow bands of optimum strength. Modern papermaking needs computer control to meet these narrower operating conditions. It is necessary to adjust for fluctuating bicarbonates in the fresh water or the effects of whitewater constituents or for the changes in temperature. Then the cheap alumina floc is a good source of cationic charge and more expensive cationics are not justified.

Mannogalactans—The anionic guar or locust bean gums increase bursting strength in papers for which other additives are not beneficial. Amounts as low as 0.05–0.1 per cent have been effective, probably because of more uniform formation. The better distribution of bonds will reduce the number of weaker areas in the paper between the well-bonded fibres.

The gums have a backbone chain of rather rigid rod-like mannose units, with short galactose side chains. The molecular weight at 250 000 is also similar to that of polyacrylamide. The gums are highly hydrated and hold this hydration more tightly than free water during drying—Kesler.[52] Leech[53] found that beaten long fibres will sorb 8.8 per cent of gum strongly: even prolonged washing did not remove the gum. Russo & Thode[54] find that gum molecules are attracted to the fibre by Van der Waals forces: other gum molecules will be attached to the first layer. This would explain the very large amount of gum that can be sorbed. Papermills cannot afford more than a few lb mannogalactan per ton pulp at 32 cents/lb. Larger amounts slow down the drainage and any fall in production is unacceptable in large production units. Swanson showed that as little as 0.07 per cent gum retained on the long fibre is effective. Leech had found that 60 per cent of the benefits from mannogalactan is due to improvement in the strength of the bonds at the fibre-to-fibre contact area. Campbell forces during drying might move the small amount of well-dispersed highly hydrated gum molecules towards these areas. Sorption must be accomplished quickly, since the time interval between addition at the head box and the dryer section is quite short at 1 500 ft/min (25 ft/sec), which is roughly one half the distance in the forming area on the wire. The rather low retention of these gums and the inability to increase production by faster drainage on the wire seem to be overcome with cationic gums. The available products are expensive at 45 cents/lb, but a more economical solution may be available.

Cationic starches—Compared with essentially unbranched polyacrylamide and mannogalactan, both with short side chains respectively of amide and of galactose groups, native starch is more complex. Amylose exists in a wide range of molecular weights and associates upon retrogradation. Amylopectin contains large branches.

A highly dispersed starch produced by heat and shear treatments in jet cookers of recent design will increase strength better than the old batch cooking with a loss of colloidal quality upon ageing. The retention of jet-cooked starch on a modern fast machine is very low. The gain in strength is then often insufficient, mainly because of the small amount that is distributed in an effective manner through the paper.

Retention was improved by the now abandoned soap-amylose reaction—

6—C.P.W. II

Houtz[55]—or by cationic alumina in the Rowland process.[56] It should be recorded that remarkable gains in strength were obtained by the writer and others on commercial papermachines, but the control of alumina chemistry in the Rowland process in 1935 was too primitive to maintain the difficult optimum conditions. The molecular weight of native amylose and amylopectin is in the range where polyacrylamide acts as a flocculating retention aid. Swanson[57] points out that starches 'flocculate less highly beaten fibres and produce poor sheet formation'. Unlike gum, starch does not improve strength by better bond distribution. A carboxymethyl ether of starch described below is designed to overcome this deficiency in formation.

The pioneering work of Caldwell & Wurzburg[58] and Paschall[59] created cationic starches to improve retention of starch for strength and of fillers for greater efficiency. It is very costly to dry gelatinised starch for shipment. Therefore, most converting by starch producers must be done with starch in ungelatinised granule form. Caldwell introduced a tertiary amine hydrochloride group through an ether linkage, probably on the primary hydroxyl of the starch molecule. A very low degree of substitution (0.03), corresponding to 0.22 per cent nitrogen, is usually applied to native corn starch. The reaction product of epichlorhydrin with trimethylamine in Paschall's process produces a starch ether with a quaternary amine. Cationic starches can be prepared from potato or other starches or starches degraded to a lower molecular weight. It appears that a higher molecular weight produces higher strength.

Moeller[60] reviews the amounts of cationic starch that are sorbed in proportion to the available fibre surface area under laboratory conditions. Considerable evidence shows that 5.5–7.5 per cent are retained very firmly and cannot be removed by boiling water or similar procedures. As shown by Linke,[50] the gain in strength levels off at 1.0–1.5 per cent addition. McKenzie[61] found a retention of 46 per cent for cationic amylopectin on unbleached pine kraft pulp, which is probably a high value compared with high speed papermachines. It is likely that 0.5 per cent of cationic starch is retained; in the laboratory, 5.5–7.5 per cent was sorbed. Moeller suggests that only the cationic starch drawn into the fibre bonding areas is useful. McKenzie[61] shows that the solubles separated from a cationic wheat amylopectin upon mild cooking to 65°C produced in paper twice the bursting strength of the insoluble fraction. Cushing[62] speculated that fresh jet-cooked starch might contain single molecular chains. Their poor retention has led to an application of cationic starch in mainly a macromolecular form. The lightly treated corn starch of high molecular weight is cooked under conditions that maintain the cationic charge. Dispersion effects caused by temperature and shear must be limited. The cooked cationic starch still contains

fragments. Cationic starch swells to a volume eight times larger than does ordinary starch, which helps its retention.

McKenzie[61] presents valuable data to show the dependence of the percentage gain in burst factor upon the degree of existing contact area before the addition of cationic starch. At 679 CSF, the burst factor was raised from 52 to 80—that is, by 54 per cent. The percentage gain was only 9.4 per cent at 304 CSF, when the burst factor changed from 85 to 93. A typical mill result is the 10 per cent change in bursting strength—from 109 to 120 lb/in². The parallel increase in speed from 980 ft/min to 1 060 ft/min is significant, since it raised production on a kraft liner machine by 37 tons/day.

Moeller[60] hypothesises that 'the highly cationic starch would be drawn preferentially to the most anionic portions of the fibre. Areas containing hemicelluloses exhibit a higher degree of anionic activity. The cationic starch would then be concentrated in the hemicellulose fraction of the fibre.'

Rounsley[64] has developed a new equation for the adsorption isotherms for the first layer of water, which is held very tightly and for the second to fifth layers of a looser attachment. In a second study[65] of the vapour transport through paper, a more comprehensive equation for permeability was established, using the following nomenclature—

A = area of adsorbing surface
$\bar{A}$ = amount of vapour adsorbed
A_0 = amount adsorbed in first layer per unit weight of adsorbent
B = amount adsorbed corresponding to a monolayer, lb adsorbed/lb adsorbent
C = partition function for adsorption energy
D_a = diffusion coefficient of adsorbed layer (containing correction for linear flow through superfacial area)
D_p = diffusion coefficient in pores
D_v = diffusion coefficient for adsorption and desorption (containing correction for interfacial area of adsorbed layer)
F = free energy (Gibbs)
k = Boltzmann constant
K = constants
n = number of layers
N_0 = number of adsorption sites
N_1 = number of molecules adsorbed in first layer
p = pressure or partial pressure of vapour
p' = vapour pressure from adsorbed molecules
p_0 = saturation pressure of vapour
P = permeability in adsorbed layer, usually expressed as vapour flow per superfacial area per unit pressure gradient
P_c = combined permeability for adsorbed flow, including adsorption and desorption resistances

P_0 = total permeability
P_p = permeability for pore flow
P_v = component of permeability caused by adsorption or desorption
T = temperature
x = relative partial pressure equal to p/p_0
y = distance through barrier

Rounsley[66] discusses the sorption of 7–8 per cent of starch or manno-galactan molecules and the movement to fibre contact areas as follows.

The permeability of a physically adsorbed material may be expressed by—

$$\frac{KTN_0^2C^2x(x-x^n)}{p_0K_3A[1+(C-1)x][1-x]^2}$$

This indicates that the permeability is strongly influenced by the constant C, closely related to the amount of chemical bonding of the primary layer, but it is the subsequent layers that migrate.

Although there is considerable evidence that the primary adsorbed starch is chemically held to the fibres, additional adsorption may occur in secondary layers long before the first layer is complete. It may be shown that, when such multi-layer adsorption occurs, the outer layers are highly mobile. For tightly held primary adsorption as with starch on cellulose, the amount of secondary adsorption is small, but mobile.

It is not strange to compare multi-layer with capillary migration. The forces causing motion in both cases arise from mutual attraction of the adsorbed molecules. Motion in any case is toward the points at which the water is being removed by evaporation. This is at the points of greatest curvature of the liquid/air interface, because of the increased vapour pressure there. The curvature is greatest near where the fibres touch.

Anionic starch derivatives—Oxidised starch or starch acetate esters or carboxymethyl ether starch are other dry strength additives. The treatment with sodium hypochlorite introduces a large number of carboxyl groups, which give a highly anionic charge to the oxidised starch. In Cushing & Schuman's experiments,[67] an amount of 0.01 per cent oxidised starch retained in the bleached sulphite handsheet raised the burst factor by 1.64 per cent, whereas starch acetate was only half as effective, with a gain of 0.87 per cent and hydroxyethyl starch produced the lowest strength increment. This confirms that oxidised starch can increase strength, but its retention is very poor. Similar to dialdehyde starch, cationic alumina does not suffice to raise retention.

The carboxymethyl starch ether is produced by a reaction of the un-gelatinised starch with sodium monochloroacetate. Kesler & Hjermstand[68]

find that this product is retained to a high degree and 'it is attracted to the glued area (fibre contact area) during drying'. The carboxymethyl group is capable of reacting with alumina and the mechanism seems to be similar to polyacrylamide retention. The increased hydration of this derivative makes it more similar to mannogalactan gums and it improves formation.

Wet strength resins

RUSSELL, KALLMES & MAYHOOD[69] examined the effects of two wet strength resins on fibre-to-fibre contacts with new testing techniques. Exposure to 10–50 per cent and 87 per cent rh illustrated the performance of a melamine-formaldehyde resin. The elastic modulus of the treated sheet was increased by 47 per cent above the untreated sheet at 87 per cent rh. Such exposure to high humidity conditions is often as important as the soaking of paper in water specified in standard wet strength tests. The melamine-formaldehyde and the polyamide amine-epichlorohydrin resins increased the dry tensile strength by 20 per cent and wet tensile fortyfold (from 45 to 2 030 and 1 630 g/cm, respectively). The degree of bonding in dry 2-D sheets was nearly alike; but, on immersion into distilled water, the untreated paper lost all its strength and the two samples with resins retained their original bond strength.

The authors concur with the views of Britt, Steenberg, Fineman and Stannet that wet strength is obtained by making the cellulose and hemicellulose bonds less sensitive to swelling in liquids. It should be added that this protection goes beyond the water resistance obtainable by very good sizing. The polyamide wet strength resins, as well as dialdehyde starches produce high wet strength in towel or other papers, without the loss of good absorbency.

Polyamide-amine epichlorohydrin—Keim[77] forms an essentially linear polyamide by reacting a saturated aliphatic dicarboxylic acid such as adipic or succinic acid with a polyalkylene polyamine (diethylene triamine or tetraethylene pentamine). The polyamide is treated with epichlorohydrin to convert the secondary amine to a tertiary and/or quaternary ammonium group. The strongly cationic product is of moderate molecular weight (2 000–5 000). The backbone chain is of a medium length and holds many reactive side chains—Schmalz.[78] Keim recommends adjusting the pH value of bleached kraft pulp with sodium hydroxide to 9.0, then adding 1 per cent (dry basis) of the resin.

Kincannon[79] reviews radioactive tracer tests with C^{14}-tagged polyamide resin* to establish single pass retention. About 50 per cent is retained in the

* The polyamide resin preparation referred to is Kymene 55

paper, 20 per cent in the fines and 30 per cent remains in the water. In a completely closed system, about 70 per cent of the addition is retained in the paper. The presence of 300 ppm sulphate ion at pH 7.0 raised wet tensile strength from 9.0 lb/in after curing (for 1 h at 105°C) to 11.3 lb/in. The addition of 300 ppm aluminate at pH 10 (negative charge at this pH value) increased wet tensile strength to 13 lb. These examples show the need for close control of application conditions to obtain the required wet strength economically. In the case of pulps low in hemicellulose, it becomes necessary to add 0.1 per cent carboxymethyl cellulose to the fibre before the cationic resin.[80] The best values indicate a ratio of wet to dry tensile strengths of 40 per cent. The influence of pulp properties is illustrated for an addition of 0.5 per cent resin. Paper from unbleached kraft pulp had a wet tensile strength of 9.0 lb/in, bleached kraft one of 7.7 lb/in, whereas bleached sulphite paper reached only 4.4 lb/in. The wet tensile strength of unbleached kraft paper in another study gave a value of 9.2 in a waterleaf sheet. Sizing with 0.075 per cent ketene dimer raised the test figure to 10.2 lb/in, although, with 2 per cent polyamide together with 0.075 per cent ketene dimer, a wet tensile strength of 12.5 lb/in was obtained. A levelling off in strength was observed for cationic urea-formaldehyde (UF) resin: even a 3 per cent addition did not raise the strength above 9.2 lb/in. It is noteworthy that the application of two cationics with a large amount of cationic polyamide and of a small quantity of cationic ketene dimer was here as effective as in the previously discussed case, in which a small quantity of polyamide resin was applied as a retention aid for ketene dimer. Good synthetic sizing increased wet strength above that provided by the resin alone; even then, the wet strength is only a fraction of the dry strength. One might have expected yet better results, since the well-cured paper with polyamide resin is very difficult to defibre completely. Böhmer[81] explains the very strong bonds of polyamide resin by a formation of covalent bonds with the primary alcohol of the cellulose molecule. The degree of self-polymerisation (cross-linking) is still being debated. The polyamide resins are recommended for absorbent tissues, towels, diapers. Amounts as low as 0.1 per cent are beneficial in linerboard. Sufficient wet strength is obtained, better drainage on the wire has been noted and, in absorbent grades, the harshness caused by alum is avoided. Increases in dry strength have been reported for bleached kraft pulp. The absence of alum does provide better resistance against ageing. No information could be obtained for the distribution of the polyamide within the paper.

Melamine-formaldehyde—High efficiency melamine-formaldehyde resin was invented by Maxwell[82] and elucidated far more broadly and in depth than for other additives by Linke and co-workers. The use of 1–7 moles

additional formaldehyde to the standard melamine-formaldehyde (tri-methylol melamine*) improved wet strength by 27–39 per cent. At an addition of 0.5 per cent, the new product gave a wet tensile strength of 6.6 lb/in, instead of 4.75 lb/in for regular melamine-formaldehyde (MF) in cases of a closed whitewater system with a content of 200–300 ppm sulphate ions. The MF resins make the fibres hydrophobic and reduce the drainage rate. A
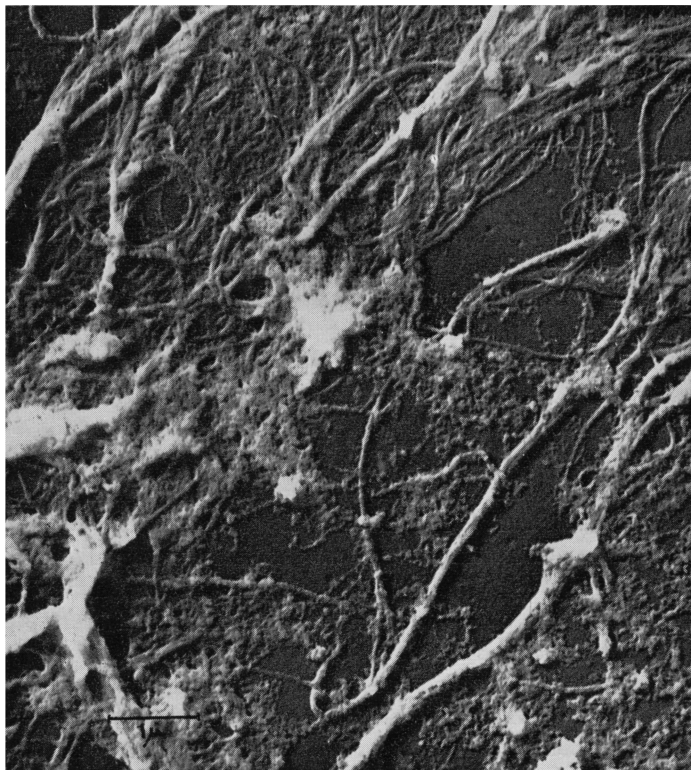
Source: American Cyanamid Co.

Fig. 7—Melamine-formaldehyde resin

curtailment of refining permits production to be maintained at the same rate as for paper without MF resin. A noticeable improvement in dimensional stability will be obtained. Certain office copy papers maintain their softness and sufficient dimensional stability by such minimum refining and treatment with resin. Large tonnages of military map paper were made with MF resin

* The preparation referred to is Parez 607

and withstood severe wet and dry folding and tearing, though their dimensional stability became poorer. An untreated rag paper had an MIT (dry) folding strength of 1 400, which was raised to 4 400 with 3 per cent MF resin. Currency paper contains MF resin to increase folding strength and resistance to splitting by forgers. On dry boards, an increase in ring crush of 41 per cent was obtained. Maxwell[84] reviews the need for aluminium sulphate and sulphuric acid to provide sufficient acidity at pH 4.5–5.0 for rapid curing by condensation of the resin. Curing at 260°F for 1–2 min at pH 4.5 is recommended. A lower pH value will provide even better curing, but reduces dry strength too much.

The loss of absorbency of paper by MF resin is reduced, if alum is replaced with hydrochloric acid. The MF colloid particles will be of 60–70 Å size, if prepared under controlled conditions for hydrochloric acid and resin concentration and upon proper ageing.[85] Landes[85] mentions a diameter of 8–10 Å and a build-up of monomers to a length of 100–200 Å. He observed their collection 'on small fibrils of the same magnitude'. MF particles were noted also around fibrils that were not yet separated from the whole fibre.

No instance of continuous filming by MF could be demonstrated. The electron micrograph supplied by Linke[86] shows fibrils and small particles of the resin colloid. Electron micrographs by Dixon et al.[87] show resin particles of 100–200 Å attached to the surface of the fibrils. Linke calls attention to the three-dimensional network present. Swanson[88] asks if the retention process fractionates the polymer into effective and ineffective parts. In his study with Becher & Hoffman,[73] the low molecular weight fraction of a cationic UF resin was removed and the remainder was applied to bleached sulphite pulp from which the fines had been separated. Even under the best conditions of agitation and diffusion, the retention was at best 15 per cent and 7–11.5 per cent for a MF resin.

Linke[74] shows for bleached northern kraft pulp (beaten to 500 CSF with the usual retention of fines), a direct relationship between wet tensile strength and retention. A constant amount of MF or high efficiency MF resin was added and the concentration of sulphate ions was varied. A retention of 20 per cent giving 2.0 lb/in wet tensile strength could be raised to 70 per cent retention with 9.0 lb/in tensile strength. The data for high efficiency MF were parallel with those for MF, but produced better wet strength in spite of poorer retention—probably by more effective cross-linking. Linke found that the highest retention and best wet strength were obtained at a sulphate ion concentration just below one that precipitates the polymer from solution. Such precipitation begins at 300–500 ppm sulphate ions. After precipitation, the resin aggregates cannot diffuse to the fibre surface and the distribution and reactivity of the sorbed units on the fibres is poor. The high efficiency

resins are probably more linear than regular MF resin. Linke suggests that a linear resin may be more efficient weight-for-weight than a branched one. 'In a branched structure, a larger fraction of the molecule or its functional groups would probably lie off the surface of the absorbent and would be unavailable for bonding. High cationic charge must be present for good retention and wet strength and the decrease of the charge by sulphate ions and ageing can be controlled by control of the concentration of resin and of hydrochloric acid during the storage of the colloid.'

Maxwell[82] presented graphs showing much higher wet strength with highly beaten pulp than for moderate or unbeaten pulps. It appears that tighter fibre-to-fibril networks and the colloid's shape, charge and double-layer conditions control retention.

A protection of fibre-to-fibre bonds by the cross-linked, cured resin requires their presence near the crossover points. The cationic resin is of little value, if it is deposited in small patches at anionic sites along the free fibre surfaces, provided the fibre remains too far distant from the next fibre for hydrogen bonding after surface tension and Campbell forces have exerted their effects. MF resin will make the unbonded fibre hydrophobic; polyamide or cationic UF resins will be wasted unless they are transported to fibre bonds. The addition of cationic resins just before the head box is currently preferred for superior distribution throughout the whole furnish, but this approach becomes increasingly inefficient as the papermachine speeds up. A better application is needed to meet marketing goals at acceptable costs.

Urea-formaldehyde resins—Brent, Drennen & Shelley[89] and Hill[90] review the available information on UF wet strength resins. Representative strength tests based on resin retained within the paper are given by American Cyanamid.[91] They show that anionic resin is preferable on unbleached kraft pulp, because of its low cost and adequate wet strength; cationic UF products are more effective on other pulps. Useful information can be obtained from the pertinent patents. Tetraethylenepentamine is used by Suen & Daniels.[92] Keim reacts triethylenetetramine[93] or guanidines[94] and suggests an attachment to the fibre by mutual attraction between negative cellulose and positive resin. This is claimed to be superior to the previous mechanical entrainment or to precipitating agents 'to fix resin on the fibre'. Acidity from aluminium sulphate and sulphuric acid or with hydrochloric acid is required for curing. Cationic UF resins cure more slowly than do MF resins, but more rapidly than anionic UF resins. Two- and three-dimensional cross-linked methylol groups on one chain combine with 'nitrogen-bound hydrogen' on another chain.[89] No data on the charge

density are available. Resins of higher molecular weight are retained better and give higher wet strength. Insolubility in water is one obvious limit and an increase in gelling tendency with concentration demands that the resin be shipped at lower concentration, with a consequent increase in shipping and storage costs. Retained amounts as low as 0.2 per cent are worthwhile in kraft pulps, but not higher than about 3 per cent cationic UF to avoid filling up of felts. Prince[95] points out that a partially gelatinised UF resin will plug wet felts, which results in serious non-uniformity in moisture content across the web. Inefficient operation of converting machinery is caused by mechanically imperfect rolls.

Hill[90] illustrates the effect of molecular weight for anionic UF resin. The retention of the low molecular weight fraction was poor at 12 per cent and the ratio of wet to dry tensile strengths was 8.0 per cent. The high molecular weight fraction had a retention of 70 per cent and a strength ratio of 20 per cent. Nevertheless, the wet strength per unit of the retained resin was about twice as high for the low fraction.* The anionic UF works well on unbleached kraft bag paper. On well-washed pulp, a wet tensile strength of 6 lb/in was obtained, which dropped to 4.0 lb/in with a residual of 5 per cent black liquor solids on oven-dry pulp. The wet tensile strength dropped from 8.0 lb/in for well-washed pulp to 3.5 lb/in at a content of 7 per cent black liquor solids.[91]

The UF as well as the MF resins increase the strength of dry paper in the z-direction. The higher tensile strength or the better wax pick or the better plybond and folding test figures have not yet been considered sufficiently in regard to the mechanism of wet strength. Previously, the absence of changes of dry strength in the machine- and cross-directions was considered proof that few additional bonds are formed by resins.

Cationic dialdehyde starch—Borchert & Mirza[83] review the development of temporary wet strength. Starch oxidised with periodate receives a treatment with one of three cationic agents: better retention and wet strength are obtained. The dialdehyde is attached to cellulose by a hemiacetal linkage. The wet strength is ample for absorbent papers and their absorbency is not reduced. The product is in commercial use and fewer wet web breaks are reported because of a better fibre bond distribution.

Cationic versus anionic latices—Anderson & Stannett[96] demonstrate that a large amount of a cationic product, although helpful in retention, is not always beneficial in strength development. The anionic ethyl polyacrylate in unbleached kraft pulp gave a 40 per cent higher dry bursting strength, a

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* Taylor's replotting of these data is presented on p. 735

130 per cent higher wet bursting strength, a folding strength of 1 320 (compared with 380) and a 25 per cent lower tearing strength than did the cationic product. The cationic latices covered the fibre with many extremely small particles, which made the fibres hydrophobic and interfered with fibre-to-fibre bonding. The anionic latices precipitated as distinct particles of varying size, but still left uncovered areas suitable for fibre bonding. Swanson's[97] observation that emulsifiers detract from bonding did not apply in this case. The authors present an electron micrograph to show several aggregates of anionic latex and 'alumina' near fibre contact areas of approximately 100 μ diameter. This waste of expensive latex might explain why 14 per cent latex had to be supplied when other additives must be effective at 0.3–2 per cent levels.

Effect of fillers

Observations on formation and drainage—Byron Baker[98] studied several papermachines producing uncoated letterpress paper with 22–30 per cent of filler at the reel. A mixture of clay and calcium carbonate was used. He found a relatively high freeness of 60 sec for the repulped wet paper from the couch. The stock from the head box was very slow in drainage (Williams freeness tester) ranging 200–2 000 sec. A very large amount of filler had to be used in the stock slurry to the wire, because of very poor single pass retention and its consistency had to be held relatively low to obtain good formation. Therefore, the volume of the stock to be drained on a given forming area was very large and the slurry with its high excess of filler drained slowly as indicated by the freeness test. This illustrates how a fairly easy draining mixture of 30 per cent filler and 70 per cent fibre at the couch becomes a drainage problem, owing to poor filler retention.

The machine coating of these large orders of magazine paper has minimised the problem, since only 5–15 per cent filler are now required ahead of coating or surface sizing. Well-designed papermachines with ample drainage area can handle relatively free stock from the head box carrying 5.0–14 per cent (at the reel) in filler, without adjustment in speed and with minor changes in couch vacuum. The tray water consistency was doubled, however and formation became slightly poorer with the change from 5 to 14 per cent filler, which is probably in line with the higher consistency from the head box. On other machines making white papers, retention aids are helpful in reducing the large volume of whitewater that is high in filler content. Various polyacrylamides of very high molecular weight compete for this duty with polyethyleneimine products or with polyamine-epichlorohydrin and cationic starches. Older materials such as Sveen glue or activated silica are less popular, since they provide only filler retention, whereas the new chemicals increase

drainage by flocculating fibre fines upon long fibres. This increases the porosity of the web, which drains faster on the wire and will dry more readily.

Mardon[99] shows that an addition of 8 per cent whitewater fines to a furnish of 540 CSF with a drainage rate of 7.5 sec lowered the freeness to 385 CSF and raised the drainage time to 10.75 sec. A flocculation of the fines as pictured by Linke[51] or a deposition of the fines that are higher in anionic charge than the long fibres because of cationic retention aids would explain the observed improvements. Hinton & Quinn's[100] measurements of electrophoretic mobility and dye absorption on the fractionated long fibres and the fines are very instructive.

Effects of wet pressing—Very few studies are available to show the effects of additives in wet pressing. Table 4 by McCann[2] illustrates the increase in burst factor, breaking length and MIT fold by wet pressing without rosin and alum and at two levels of sizing. It is known that suction presses remove some filler. Bursting strength is slightly increased in line with less filler. Swanson[101]

TABLE 4—EFFECT OF WET PRESSING ON UNBLEACHED SOFTWOOD KRAFT
PULP AT pH 9.5

Test value	Description		
	Pulp alone	*Minimum rosin*	*Normal rosin*
Rosin, per cent	None	0.05	1.0
Alum, per cent	None	1.43	1.91
pH value with sulphuric acid	None	5.5	5.5
Wet pressing, lb/in²	10	10	10
	35	35	35
	60	60	60
Burst factor	46.7	45.6	43.7
	53.4	52.7	46.0
	53.0	53.2	47.5
Tear factor	164	170	160
	141	135	147
	125	126	142
Breaking length, m	6 795	6 822	6 434
	7 688	7 483	6 846
	8 210	8 003	6 764
Stretch, per cent	2.9	2.8	2.8
	2.7	3.0	2.8
	2.8	3.0	3.1
MIT fold	496	355	379
	677	442	356
	925	486	432
Bulk, cm³/g	2.9	2.17	2.05
	2.7	1.81	1.85
	2.8	1.70	1.75

Data by McCann[2]

points out that few fibre bonds are formed during wet pressing, owing to springback of the fibres upon release of the pressure.

Wenzl[102] gives data on the effect of pressure in wet pressing upon the total void volume and the volume of pores. At a pressure of 0.15 kg/cm^2, the pore volume was 48.8 per cent, which was reduced to 2.6 per cent under a pressure of 3.5 kg/cm^2. Corte's[103,104] intensive studies on the porosity of 2-D and multi-planar sheets must be examined.

Washburn & Buchanan[105] present very good pictures taken with the scanning electron microscope on the effect of wet pressing upon beaten fibres.

Ratio of strength loss divided by gain in scattering coefficient—Brecht & Pfretzschner[106] showed in a broad investigation that the decrease in dry strength properties with an increase in the content of filler in paper was not alike for all fillers. The tests were made at constant sheet substance, which means a decrease in the amount of fibre proportional to the increase in filler content. Table 5 shows that bursting strength losses at a constant 10 per cent filler content varied from 10 per cent for calcium sulphate (anhydrous) to

TABLE 5—EFFECT OF FILLERS ON THE STRENGTH OF PAPER CONTAINING ALUM

Decrease in strength property from the value without filler, per cent	*Filler content in paper, per cent*		
	10	*20*	*30*
Loss in tensile strength—			
Gypsum filler	10	24	40
Clay filler	17.5	40	52.5
Loss in bursting strength—			
Gypsum filler	10	25	40
Clay filler	28	46	63
Loss in tearing strength—			
All fillers	7.5	23	33
Loss in Schopper folding strength—			
Zinc sulphide filler	43	76	90
Clay filler	73	93	98

Data by Brecht & Pfretzschner[106]

28 per cent for clay, if alum was used. Steele[107] applied the Kubelka-Munk theory to paper and suggested the scattering coefficient as a measure for an appraisal of the contribution of the filler to the opacity of paper.

Culp & Kelley[108] related the percentage decrease in bursting strength to the percentage gain in scattering coefficient (100S) of paper with filler and sheets without filler. Table 6 shows that a large loss in bursting or folding strength, together with a low gain in scattering coefficient, indicates a filler of low value for most papers. Such filler would be useful only when it is low

TABLE 6—PIGMENT AND PAPER PROPERTIES
(pH 4.5 with aluminium sulphate)

Pigment	Refrac- tive index	Reflectance, 457mμ	Abrasiveness, mg	100 S_{pigm}.	$\dfrac{\Delta Burst}{\Delta 100S}$
Coating clay	1.56	84.5	2–7	14	0.70
Precipitated silica	1.45	96.0	5–6	25	0.80
Alumina hydrated	1.57	99.2	6	29	0.40
Anatase titanium dioxide	2.55	96.0	12+	43–51	0.40
Rutile titanium dioxide	2.70	96.0	9+	54–68	0.3–0.4

in cost, very white and could be applied in a paper or board for which a loss in bonding strength was not objectionable. Hughes[109] provides other examples.

A paper of light substance for printing with very tacky printing inks in an offset press requires high opacity and ample bond strength in the z-direction to prevent picking or delamination. This may suggest the selection of titanium dioxide, because small quantities can provide the required light scattering. The use of a small amount such as 1–4 per cent titanium dioxide well distributed through the paper will decrease bursting strength by 4–16 per cent. This explains the ratio of 0.3–0.4 for loss of bursting strength divided by the gain in 100S. This solution of a difficult problem (high opacity plus high strength) is frequently applied, provided the profit margin of the products is sufficient to permit the use of the expensive titanium dioxide. The ratio of 0.4 is higher than desirable, but titanium dioxide in combination with the usual rosin size and alum weakens the paper considerably.

Table 7 presents new data by Hagemeyer[110] on the effects of calcium carbonate in papers sized with ketene dimer, whereby the strength loss by rosin and alum is avoided. The fairly coarse precipitated calcium carbonate of acicular shape of 0.8–1.0 μ (length as determined under the electron

TABLE 7—PIGMENT DIMENSIONS AND PAPER PROPERTIES
Semi-bleached kraft with ketene dimer and polyamide resin

Particle shape	Dimensions, μ	100 S_{pigm}.	$\dfrac{\Delta Burst}{\Delta 100S}$
Acicular calcium carbonate	(0.4–1.20) × (0.1–0.2)	30.2	0.2
Acicular calcium carbonate	(0.8–1.0) × (0.15)	30	0.17
Rhombic calcium carbonate	0.035–0.040	27.7	0.24
Rhombic calcium carbonate	0.10–0.35	35.9	0.17
Non-crystalline calcium carbonate	0.1–2.5	24.4	0.275

Data by Hagemeyer[110]

microscope) lost 30 per cent in burst factor in a sheet with 10 per cent filler. The ultra-fine and rhombic product designed for incorporation into rubber was difficult to disperse. It had to be used in an agglomerated condition. Therefore, its opacifying power was no better than the natural calcium carbonate with rounded corners produced by ballmilling. The loss in strength of certain calcium carbonates and the good gain in 100*S* in an alkaline paper result in ratios different from those for acid sheets.
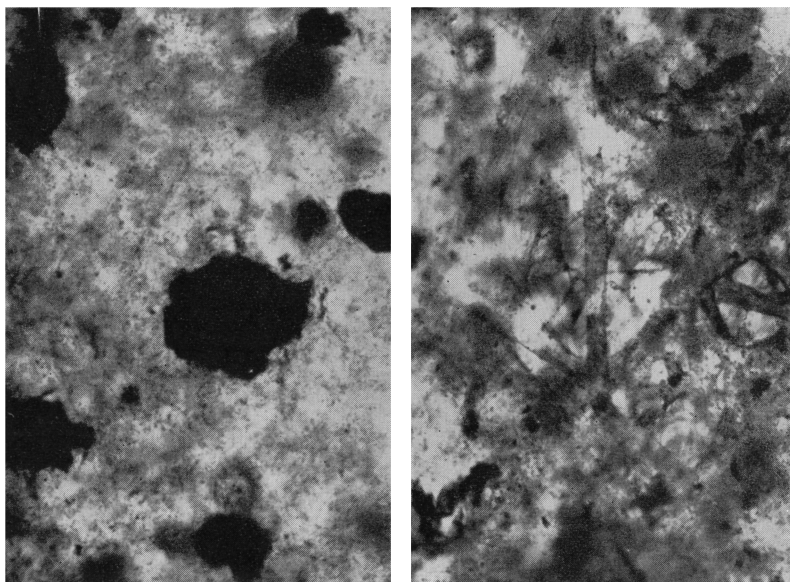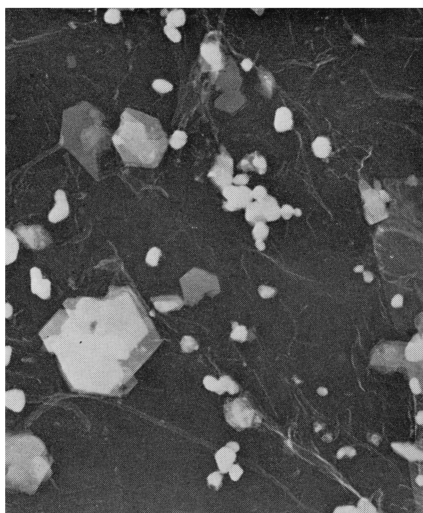

Source: O. Uhrig, The Mead Corporation, Central Research Laboratories

Fig. 8—Flocculated filler [× 83]   ***Fig. 9***—Reduced pigment aggregation [× 83]

Another pigment of very small ultimate individual particles (0.03 μ), but agglomerated to loose clusters of 0.20 μ is suspected of lowering bond strength. Arvold[111] reports that a material of composition $CaO \cdot 4SiO_2 \cdot 3H_2O$ formed in the presence of fibres from sodium silicate and calcium chloride reduced the fibre bonding to a level that made the paper unsatisfactory for offset printing and could not be remedied by heavy surface sizing.

All these pigments that unbond paper to a degree that sheet offset or web offset printing becomes defective are not high in abrasiveness as tested on the Valley abrasion tester by the loss in weight of a papermachine wire. It is conceivable that this is due to a very large number of very small particles that interfere with hydrogen bonding frequently enough to lower strength.

The single trial with ultra-fine calcium carbonate of 0.040 μ ultimate size, which was used in an aggregated state in the presence of alkaline sizing together with a polyamide amine epichlorohydrin resin, did not lower bursting strength excessively. This sheet was not tested by offset printing. Both the wet strength resin and the cationic starch in the ketene dimer size might well have compensated for a drop in z-direction strength. The other pigments that have been criticised for an unbonding action were used with rosin size and usually with high amounts of aluminium sulphate necessary to neutralise calcium compounds.

Source: D. C. McIntosh & D. B. Uhrig, The Mead Corporation, Central Research Labs.

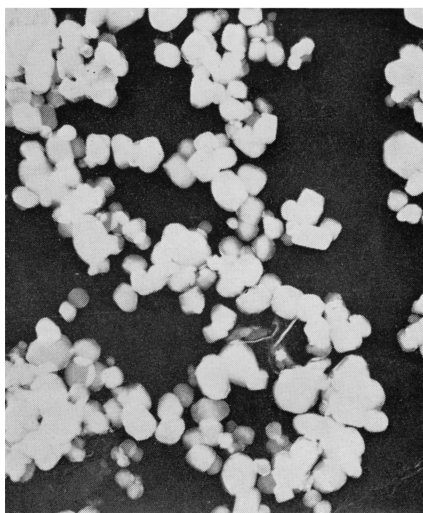*Fig.10* —Well-dispersed titanium dioxide in paper [$\times$ 17 250]   *Fig. 11*—Typical distribution of dispersed titanium dioxide in paper [$\times$ 13 150]

Mays [112] applied electron micrographs of ultra-thin (400–800 Å) cross-sections to an investigation of the distribution of silico-aluminates and clays within newsprint. Mays confirms that the strength properties of the paper are very important in printing works. It should be noted that letterpress printing is less severe in its z-direction strength demands than is offset printing and that news ink is even less tacky than standard letterpress inks. Mays also restricted the filler content in the newsprint to a low amount of 2–4 per cent, whereas offset sheets frequently contain up to 15 per cent filler. The electron micrographs show that 'a filler particle of 0.015–0.050 μ size can easily infiltrate and fit into the capillaries of 0.08–0.5 μ size between the fibrils and micro-fibrils. This penetration into smaller pores and capillary slits does not affect

sheet strength.' Mays specifies that the chemical composition of the filler must be carefully controlled to avoid 'scale-forming components'. Possibly, this previously poorly controlled feature explains the loss of bond strength with other pigments.

TABLE 8—FILLER DISTRIBUTION PROFILE BY SHEET SPLITTER

Material tested	Ash content by quarter sections, per cent				Total filler by quarter sections, per cent			
	Top side	Top middle	Wire middle	Wire side	Top side	Top middle	Wire middle	Wire side
Internal head box	8.9	9.0	9.1	4.7	28	28	29	15
Improper spray	11.2	7.2	1.4	1.0	53	35	7	5
WMU NP trial*	4.8	4.8	5.3	4.2	25	25	28	22
Handsheets	2.7	4.0	4.4	3.9	18	27	30	26

* Western Michigan University newsprint trial

Voet[113] reports that newsprint has a high void fraction of 0.60. Mays[112] observed in a newsprint of 82 μ thickness various cavities, some of 5 μ height and 8 μ length, of undetermined width because of a ultra-thin cross-section. Other voids had dimensions of 2 $\mu \times 9$ μ or $2\frac{1}{2}$ $\mu \times 2\frac{1}{2}$ μ. Slits of 1 μ depth and 3 μ length were noted. Capillaries of 0.25 μ and 0.5 μ diameter were seen. Mays[114] in an interim report compares the internal addition of silico-aluminate with the spraying of pigment at the wet end. Table 8 gives the distribution of filler in the four layers obtained with the sheet splitter.[115] Tests with the mercury intrusion porosimeter are presented in Fig. 12 and 13.
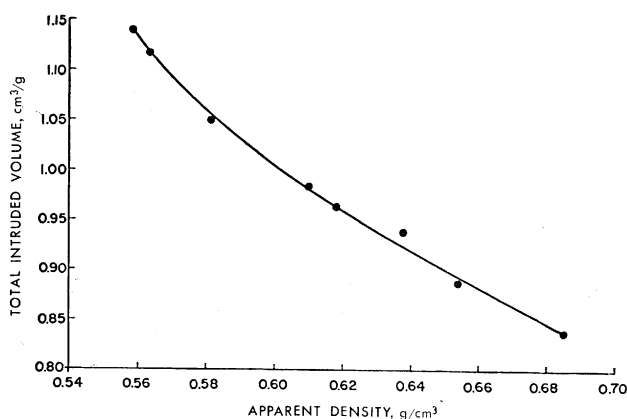

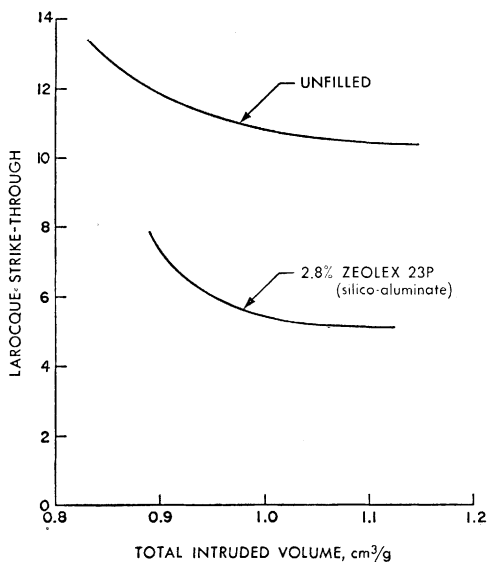*Fig. 12*—Total intruded volume plotted against apparent density

Fig. 13—Strike-through plotted against total
intruded volume, 32 lb newsprint

Scattering coefficient of pigment—Steele[107] determined the scattering coefficient of the pigment (100 $S_{pigm.}$) as it exists in a paper by optical tests of the sheets with and without filler. This assessment of the contribution of filler to opacity was first applied by a few papermills,[108] but its value is now recognised generally. Wide variations were observed for anatase titanium dioxide with values of 22–51.[108] Riches[117] showed in laboratory work that the 100 $S_{pigm.}$ was highest at 1.0 per cent titanium dioxide in the sheet (for example, 51 for anatase and 68 for rutile), yet the opacifying effect at 12 per cent in the paper was much reduced (anatase 39 and rutile 54). Kelley's[118] handsheets with anatase indicated an even better 100 $S_{pigm.}$ value of 98 at 1.1 per cent titanium dioxide in the paper, which dropped off to 38 at a content of 31 per cent anatase in the paper. These new observations show that increasing the amounts of titanium dioxide decrease their contribution to opacity. Not only is titanium dioxide very expensive, but 2 units can be less effective than one, if used in a crowded system.

Inefficient use of titanium dioxide has occurred if an identical grade of paper needs twice as much pigment to be retained within the paper from one papermachine than it does from another machine. In several such cases, the papers were nearly identical in opacity, reflectivity, density, smoothness and furnish composition. The machine that required the doubling of titanium

dioxide was also deficient in single pass filler retention. In addition to a poorer $S_{pigm.}$ value, because of the larger amount in the paper, the retention of mainly coarser particles harmed the opacity.

Johnson[38] showed that the deposits of titanium dioxide particles on nylon fibres were not uniform. 'Some areas of the fibres have a coating of particles, many particles thick, while in some cases there are areas immediately adjacent
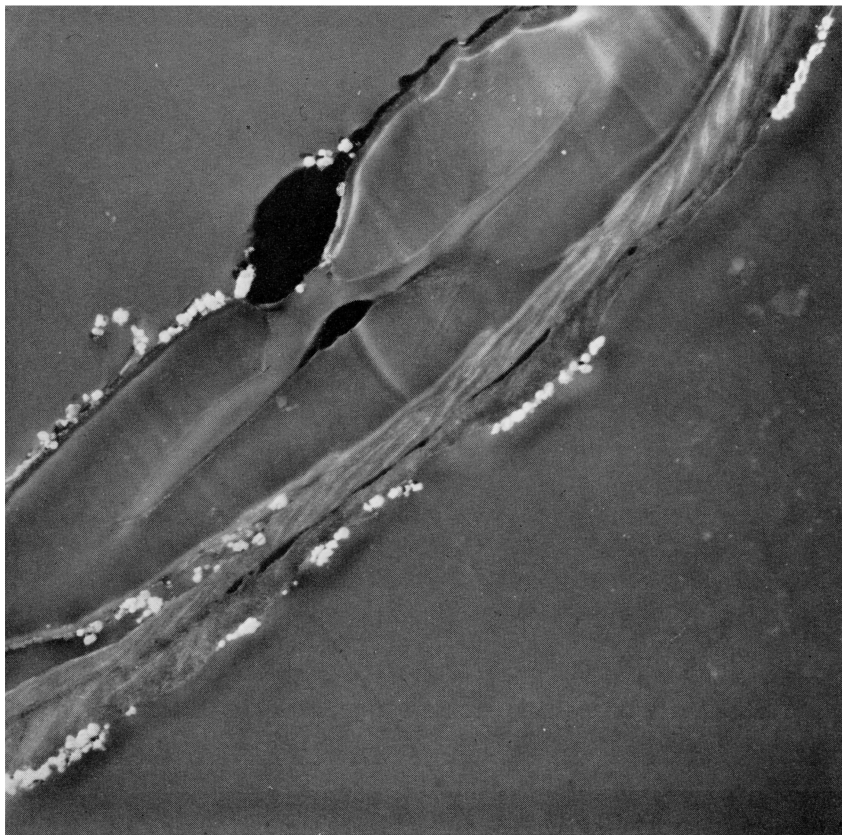

Source: D. C. McIntosh & D. B. Uhrig, The Mead Corporation, Central Research Laboratories

Fig. 14—Good titanium dioxide efficiency: ultra-thin cross-section of paper with clay and titanium dioxide [× 13 250]

that are completely barren of particles.' Haslam[119] noticed that zinc sulphide particles tended to collect on particles already attached to the fibre rather than on bare areas. Johnson reports that, upon a certain retention of titanium dioxide, the solid fraction of his sheets was changed by only 3 per cent, but a 65 per cent increase in the filtration pressure drop occurred in a trial run. This indicated that the presence of titanium dioxide particles on the surface of the fibres greatly influenced the flow pattern around the fibres. Han[120] reviewed Johnson's work and more recent studies at the Institute of Paper Chemistry. He confirmed the agglomeration of particles with each other or their adherence to solid surfaces when they came into close proximity,

Van der Waals–London attractive forces being stronger then than repulsive forces. The adherence of filler particles on the fibres depends on the hydro-dynamic forces. This explains the decrease in single pass retention on very fast papermachines equipped with table rolls. The judicious application of

Source: D. C. McIntosh & D. B. Uhrig, The Mead Corporation, Central Research Laboratories

Fig. 15—Dispersed titanium dioxide: ultra-thin cross-section of paper showing titanium dioxide round the edges of a fibre [× 5 100]

carefully adjusted foils permits improvement of the filler retention. The harmful effect of tight agglomeration of titanium particles and an elegant solution for baking enamels was demonstrated by Alpert.[121]

Whately[122] attributed the mutual attachment of dry titanium particles to high free surface energy. The observations by Stieg[123] are widely accepted.

In paint films, the individual titanium dioxide particles must be separated from the next by at least one particle diameter. All these observations in other fields show that tight agglomeration of many particles either similar to a stack in Johnson's case or as a three-dimensional pack must be less effective in the opacifying of paper. A severe case of titanium dioxide agglomeration is shown in Fig. 8. It required 4.5 per cent titanium dioxide within the sheet to obtain the specified opacity and the bursting strength was lowered. Another procedure permitted reduction of the aggregate size, whereupon only 1.5 per cent titanium dioxide was required and the bursting strength was higher (Fig. 9). Similar aggregates of titanium dioxide are shown by Newman & Fletcher with microradiographs.[124]

Our latest work is illustrated in electron micrographs at $\times 23\,000$ magnification. This proves that, in paper of 45 lb (25 in $\times$ 38 in, 500s) produced at 1 100 ft/min, it is possible to avoid agglomeration. Individual titanium dioxide particles of 0.25 μ are clearly visible. Several particles are present that are too small for best light scattering at a size of 0.07 μ. Very good scattering coefficients were obtained in these papers with a value of $S_{\text{pigm.}}$ for rutile of 125 and for an anatase of 95. It was demonstrated that the best tests from handsheets can be duplicated in a paper made at high speed.

Improved performance by unbonding with filler—Bauman[125] during a discussion of rotogravure printing at high speed mentioned the great importance of stretch of the paper. Ability to run the paper refers to uninterrupted operation at the printing press with a minimum of breaks per 100 rolls, an absence of wrinkles and of other defects. Newsprint, rotogravure or coated letterpress paper made from a groundwood furnish (provided pulps and papermaking are satisfactory) has the reputation of good runability. In a few cases, coated letterpress paper made from bleached pine kraft and hardwood soda pulps did not perform as well. In a co-operative programme, an intensive study of high speed printing was made during several weeks to obtain reliable evidence. Culp[126] demonstrated that a deliberate reduction in strength by filler enabled the groundwood paper to be matched in runability. The following discussion by Culp describes this development.

In the initial trial, a furnish of hardwood soda and softwood kraft pulps was substituted for the usual kraft/groundwood stock and the paper was made on the same papermachine used to make the regular groundwood sheet. This paper gave considerable trouble in the subsequent pressroom trial. It exhibited much more tendency than the groundwood paper to wrinkle in the press; the wrinkles were hard, frequently cracked open and occasionally caused a printed ribbon to snap off, shutting down the press. In addition, the printed signatures (book sections) tended to spring open after folding, which

made it more troublesome to jog and stack them into complete magazines.

Eventually, it was concluded that the critical factor to affect runability in this case was that the sheet could stretch in response to sudden changes of tension in the press.

It was noted that the ultimate tensile strength of the groundwood paper, while lower than that of the 'free' sheet, was apparently ample, since web breaks in the press were virtually never attributable to simple tensile failure of the web. It was seen also that the slope of the initial portion of the stress/strain curve was less steep for the groundwood sheet—that is, at a tensile loading much below its ultimate strength, the groundwood sheet was capable of slightly more elongation than the 'free' sheet. It was recognised that this would confer more ability to adjust to tensioning without pulling the web into hard wrinkles.

Following up this thinking, a trial of the 'free' furnish was made in which the base stock was purposely unbonded by addition of clay to the stock, in order to obtain stress/strain behaviour more like that of the groundwood paper. Since the mill had no tensile testing equipment, resort was had to the bursting test as a rough guide to the tenacity properties of the sheet for control during the trial. In the first of the trials, bursting strength had been in the range 22–24; with addition of filler for unbonding, it was reduced to about 16. The regular groundwood paper gave a test figure of about 18.

In the pressroom evaluation, the unbonded sheet showed no more tendency to wrinkle than did the groundwood sheet. It still tended to spring back somewhat after folding, but less so than before.

Tensile tests on an Instron tester indicated that the slope of the initial portion of the stress/strain curve had been changed appreciably as a result of addition of clay to the furnish. Since, for all samples, the curves showed almost negligible change of slope up to a tensile load of 5 lb/in, the nominal slope of the curve over the range 0–5 lb/in was taken as an estimate of the ability of the sheet to stretch in response to tensile loads of the order likely to be encountered in the press. Averaged results for typical samples were as follows—

Paper	Elongation, per cent
Groundwood	0.230
Groundwood-free, initial trial	0.221
Groundwood-free, unbonded	0.233

Actual web tensions in the printing press were not determined; in any case, the rate of tensioning in the press was no doubt many times that

employed in the tensile testing, in which 5 in strip test pieces were strained at the rate of 5 in/min.

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Discussion

Mr D. H. Page—Schwalbe has mentioned at a number of points in his paper the possible way in which starches and other materials improve the strength and he quotes (on page 708), 'Linke explains these gains by a "filling in between the fibrils and around the fibre-to-fibre contact points".'

About five years ago, we obtained direct evidence of the effect of starches on the contact areas. Tydeman and I took micrographs of contact areas in sheets before and after immersion in and drying from a starch solution. Typical results are given in Fig. M. These demonstrate quite clearly that a starch solution has two main actions. It fills in the contact areas and also creates bridges between fibres that were previously not in contact.

I think we can be a little more positive about the mechanism here of strength improvements attributable to additives than Schwalbe has been. This work was reported in the B.P. & B.I.R.A. *Bulletin* of June 1962.

Mr R. R. Davidson—The paper industry is the only industry I know that, when it wishes to decrease the pH value of an aqueous slurry, adds alum, not acid. This can well mean, as Schwalbe has pointed out, that in the final paper there may be an amount of alum in considerable excess of that necessary to develop the sizing.

In Fig. 1, as the rosin-alum complex concentration was increased, the strength of the paper fell and the opacity increased. The excess of alum appeared to be acting as a filler. A simple calculation shows that the alum is extremely expensive when employed as a filler in this way.

Dr H. C. Schwalbe—I have very little to say, because I agree with all these comments. I am very grateful for Taylor's study of the data by Hill. This new interpretation makes very good sense.

Hudson's contribution is most welcome. We need more discussion about the migration of these materials once they are caught. How do they move? We particularly wish to know how to get the bonding agents to the right place. At the moment, I am very much interested in synthetic fibres and the same problem exists of how to get the expensive bonding agent to the cross-over points and not to waste it somewhere else. So this is very interesting.

(a) Before immersion in starch

(b) After immersion in starch

Fig. M—Effect of starches on fibre contact areas

I am glad, too, for Page's observations. We wanted to demonstrate the location on fibres of starch or polyacrylamide, etc., but we did not know how to do this under the electron microscope. Our ambition was to show these small particles, because our general theme was (and still is) that we need to use these additives at the best state of dispersion so that only the minimum amount of starches, etc. are required.

I fully agree with Davidson and can add only one thing—that Watkins, for example (and I am sure many other experts in the rosin field), has advocated the use of sulphuric acid in addition to or in replacement of aluminium sulphate. Certainly, we know that excess alum (building up to a filler content of

4.5 per cent) is a very expensive and not very efficient loading. It will be interesting to determine the specific alumina complexes that lower paper strength.

Dr W. Gallay—There is one comment I would like to make and it is similar to that made by Page, but adds a further practical element. All of us in industry, of course, are frequently approached by our friends from the chemical industry with bottles of rather magic materials that are intended to obviate all our problems. If not actually a cure for all our ills, they are often put in the light of a broad spectrum antibiotic that will cure many of them. There is one point, however, that is usually not mentioned. It is common experience that many extraneous adhesives give good results in sheets made from unbeaten or lightly beaten pulps, but their effect progressively decreases in magnitude until it is negligible with normal beating. The explanation has been given of course by Page.

To put the explanation differently, the lack of conformability at crossover points in the case of unbeaten fibres apparently leaves room for an added area of bonding by a bridging effect. With adequate beating, however, a maximum is reached through natural bonding, which is not further enchanced by the wet end adhesive.

Dr J. Grant—Schwalbe's curves show the variation in scattering power with the percentage of filler. The curves for titanium dioxide seems to start at 1 per cent and to fall with increasing concentration. What happens below 1 per cent?

Dr Schwalbe—It is intriguing to know if this scattering coefficient can go up yet more. We have data going below 0.5 per cent and have asked, of course, what its upper theoretical limit is. I reported in the paper that the very first data in this field by Shick gave an $S_{plgm.}$ value of about 22. Then it was pushed up to 44, now we have come up to 90–100 and we have debated what would happen, for example, if 0.25 per cent was used. We have insufficient data to answer reliably.

Dr A. B. Truman—Have you any evidence of the effect of the agglomeration of filler particles, with or without the use of polyelectrolyte retention aid on the distribution of the particles in the z-direction? My own experience is that there is a tendency for something of this kind to take place, resulting in preferential deposition of filler on the top side of the sheet. I have on occasion found (by sectioning the paper) that, in a sheet of about 25 per cent average filler content, the top side sometimes has as much as 78 per cent filler content.

Dr Schwalbe—I quite agree with these statements. We have similar figures and others given at the previous symposium by Groen. There is considerable evidence available in many mills.

Mr W. F. Reynolds—In Table 3, the electrophoretic mobility of several pulps is shown after treatment with aluminium sulphate. Measurements made in our laboratory on pulp fibres (actually fines) suspended in distilled water have not indicated the fourfold difference found by Vandenberg and Spurlin on aluminium sulphate treated fibres. In the vicinity of pH 4.5, it is very difficult to control the charge on alumina floc by adjusting the pH value, owing to the fact that the potentiometric titration curve for aluminium sulphate at pH 4.5 is quite flat.

I do not wish to imply that the electrophoretic mobility of treated fibres is of little value. On the contrary, our experience has indicated that properly used, this property of fibres can be useful for monitoring the use of additives in the papermaking process. The measurement can be done almost as quickly as a simple pH determination.