

EFFECTS OF SOLUBLE NON-FIBROUS MATERIALS ON FORMATION AND CONSOLIDATION OF PAPER WEBS

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Synopsis—The effects of soluble electrolytes and certain polyelectrolytes on fibre swelling, beating rate, fibre flocculation, drainage and strength properties are discussed. Pulp fibres sorb electrolytes because of various acidic groups naturally present in hemicelluloses and lignin residues, also because of various oxidation reactions. Ion exchange reactions occur between the acidic groups and electrolytes on woodpulp, but purified pulps are much less acidic and sorb salts by means of surface reactions that are less well characterised. Dilute alkalis increase fibre swelling, beating rate and strength properties of pulps. The effects of cations vary with valency and concentration. Generally, rate of beating and strength properties are enhanced slightly by monovalent cations, retarded and reduced markedly by trivalent and quadrivalent cations, unaffected by divalent cations. Ion antagonism is observed. Electrolytes change the electrokinetic potential of fibres as expected and drainage rate of the pulp is a maximum at the isoelectric point, unless hydrous precipitates have formed by hydrolysis of the salt. The effects of surface-active agents are more complex.

Low molecular weight electrolytes have discernible effects on fibre flocculation at low consistencies (0.01–0.05 per cent) and low rates of shear, but these effects are negligible at papermaking consistencies, unless hydrolysis of the salt occurs. The effects of polyelectrolytes are pronounced under papermaking conditions and may possibly be explained by La Mer's theory of polymer flocculation.

The factors that influence retention of wet strength polymers by fibres are discussed. The rate of retention appears to be governed by a diffusional transport process rather than a molecular segment adsorption step.

The mechanism of development of wet strength apparently involves partial diffusion of the resin into the fibrous structure followed by curing of the resin, which subsequently restricts swelling of the bond region in water. Little evidence exists for the formation of chemical bonds between pulp fibres and the wet strength polymer. Very pure pulps may be an exception.

Soluble gases become insoluble during papermaking and have profound effects

upon stock preparation, drainage and formation on the machine and final sheet properties. Foam is discussed as a competition between two rate processes—the rate of introduction of gases and the rate of foam collapse. The rate of foam collapse may be increased substantially by anti-foams. A theory of anti-foam action is discussed.

Introduction

MANY soluble chemicals exist in the papermaking system either because of inadequate washing of the pulps, poor quality make-up water or because these substances are purposely added to attain specific effects. Among these materials are lignosulphonates, black liquor solids, alkalis, various organic and inorganic salts, surface-active agents, dyes, chemicals for control of slime and pitch, gases, antifoams and soluble natural and synthetic polymers. Certain of these chemicals have profound effects upon the colloidal behaviour of fibre/water suspensions and these effects, in turn, influence fibre flocculation, fibre distribution in the wet web, drainage and strength properties. Papermakers have been aware of the more obvious effects of these substances for many years and they have learned in some instances to control, tolerate or utilise them as the case requires. Chemical suppliers, aware of the large potential market presented by the paper industry, have developed numerous stock additives for various specific purposes that often add to the complexity of the system. The modern emphasis upon greater production and faster machine speeds coupled with the desire for improved quality and greater versatility of paper products have made many of the effects of these materials more critical than ever before. It is the intent of this paper to review and interpret if possible the effects of certain soluble substances upon the paper-making properties of pulps.

The interpretation and understanding of the effects of soluble materials is handicapped of course, by our incomplete understanding of the properties of fibres and paper in their absence. Nevertheless, the effects should be discussed in a logical way so far as possible. It has proved helpful to list a number of factors believed to be fundamentally important to fibre behaviour and paper strength⁽¹⁾—

Wet fibre properties or factors

Chemical and physical composition
Dimensions
Conformability or flexibility
Hydrodynamic specific surface area
Swollen specific volume
Flocculation

Dry properties of paper

Fibre strength
Bonded area
Bonding strength per unit bond area
Bond distribution (sheet formation)
Stress distribution

This is a formidable list and, of course, it is incomplete—for example, the

surface tension of water and numerous machine variables must also be considered.

It is established that each factor plays an important role in papermaking and it is expected that soluble materials will influence them. An interesting observation about the list is that none of the factors can be eliminated on the basis that it is unaffected by additives or extraneous materials in the papermaking system. It should be noted, however, that soluble substances may influence several properties simultaneously, some beneficially, others adversely. Comparatively little study has been made of systems in which the several effects have been controlled and elucidated. Until this is done, our understanding of the effects of these materials will be incomplete and inadequate. In the few cases of more thorough studies that have been made, a much clearer picture exists.^(1, 2)

The effects of soluble materials will be discussed in terms of the above factors, when possible, but will be regrouped into effects on drainage, flocculation of the fibres and the development of interfibre bonding. The literature on stock additives that affect wet and dry strength properties, surface properties, internal sizing, pitch deposition, foam troubles and optical and printing properties has been reviewed up to 1961 by Swanson⁽⁷¹⁾ and has been brought up to date and extended by Schwalbe⁽³⁾ and Higgins.⁽⁴⁾ This paper is intended to cover only soluble materials, but discrimination between soluble and dispersible is difficult in certain instances and some overlapping and duplication may occur.

Interactions of pulp fibres and electrolytes

NUMEROUS electrolytes exist in the usual papermaking system and it is expected that they should influence the chemical composition and physical properties of pulp fibres. These electrolytes arise from several sources such as the wood, the residual pulping and bleaching liquors, hardness of the supply water, certain filler pigments, dyes, alum, alkalis, acids and other added chemicals.

Among the fibre properties that may be altered by electrolytes are swelling and hydration, electrokinetic potentials, dye absorption, degree of flocculation, fibre bonding and ageing and electrical properties.

Base exchange properties of pulp fibres

It has long been known that, when neutral salt solutions are passed through filter paper, they become acidic because of an ion exchange reaction somewhat similar to what occurs with zeolites. Activated jute softens water and it appears that the action is limited to cations. This base exchange capacity of cellulose fibres is important to several industrial uses and has received considerable attention in papermaking, because of its relationship

to rosin sizing,^(5,6) dyeing,⁽⁷⁾ electrical properties of paper⁽⁸⁾ and self-sizing in papers and paperboard.⁽⁹⁾

The absorption of sodium hydroxide from dilute solution by cellulose was studied by Viewig⁽¹⁰⁾ as early as 1907 and, in the twenties, Kolthoff,⁽¹¹⁾ Lorenz⁽¹²⁾ and Neale^(12a) made critical studies of the mechanism involving relatively pure cellulosic materials. It was concluded that typical adsorption of alkali occurred at low concentrations of the order of 0.001–0.01N. In 1929, Edge⁽¹³⁾ studied the decrease in acidity and alkalinity of dilute solutions resulting from the presence of pulp. For acid solutions, the decrease in acidity was generally equal to the loss of alkalinity of the pulp ash. The removal of alkali from dilute solution did not increase the alkalinity of the pulp ash and he proposed that alkali was not absorbed as such. It was suggested that organic acid in the cellulose is responsible. Rag pulp contained an insignificant amount of the organic acid, kraft pulp a small amount and sulphite pulp a considerable amount. Acid-treated rag pulp could be washed to a neutral condition, whereas the other pulps remained persistently acid.

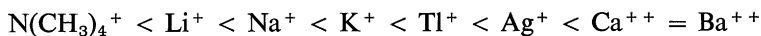
Papermakers have long known that the ease of rosin sizing may be related to the purity of the pulp. Sieber⁽¹⁴⁾ made one of the earliest studies of this observation. He noted that clear, brown solutions of sodium rosinate gradually became opalescent when placed in contact with cellulose fibres. This behaviour indicated liberation of free rosin which was attributed to preferential adsorption of the metal ion by the fibres. Bialkowsky⁽⁵⁾ studied this phenomenon quantitatively and showed that a marked relationship existed between alkali binding capacity of a pulp and its relative ease of sizing with rosin. Downs⁽¹⁵⁾ continued this work and proved the presence of organic acids in the alkaline filtrates from treated pulps. He could find no exchange adsorption between the inorganic constituents of pulps and sodium hydroxide solution at low concentrations (0.005N). Rowland⁽¹⁶⁾ incorporated these ideas with the colloidal theory of rosin sizing. It was proposed that those pulps that possess the greatest cation exchange or alkali binding capacity forced the hydrolysis of sodium rosinate to a greater degree and liberated more free rosin, which was thought to be the most effective sizing agent. Although the hydrolysis mechanism appears to be correct, the role of free rosin acid in sizing is more complex than the simple interpretation given in this early work.

McLean & Wooten⁽¹⁷⁾ also studied the characteristics of papers that cause high metal ion adsorption. These workers showed a good correlation between the ash content of paper and dielectric breakdown strength. High alpha-cellulose, low ash content papers were much better dielectrics than papers containing high ash contents such as those from unbleached kraft pulp. Acid washing of paper having poor dielectric strength reduced the ash

content and improved the dielectric properties. McLean⁽⁸⁾ suggested that acidic groups such as carboxyl, sulphonyl and phenolic hydroxyl in non-cellulosic components of the pulp are the exchange sites.

Although undissolved lignin may participate in the base exchange capacity of woodpulp, it is quite probable that hemicellulose remaining after the pulping operation also plays a significant role. Saarnio, Wathen & Gustafsson⁽¹⁸⁾ showed that acidic hemicelluloses are completely dissolved from spruce and pine woods during the sulphate process, only neutral hemicelluloses remain in the pulp; in sulphite cooking of spruce, pine, birch and aspen, part of the acidic hemicelluloses of the wood remains in the pulp and hardwood sulphate pulps also contain acidic hemicellulose. Ant-Wuorinen⁽¹⁹⁾ claims that the carboxyls on cellulose have two different levels of activity in base exchange reactions. He indicates that it is impossible to obtain cellulose entirely free of metal ions by an acid washing of the pulp followed by washing with distilled water. Some carboxyl groups appear to be such active exchangers that they scavenge traces of metal ion from purest distilled water. If the distilled water is saturated with carbon dioxide, the pick-up of metal ions is reduced, but not in Ant-Wuorinen's opinion completely eliminated. Sihtola⁽²⁰⁾ made a study of the acidity of cellulose itself or that part produced by oxidation. He concluded that carboxyl groups in the sixth position are stronger acids than those in positions 2 and 3.

Davidson & Nevell⁽²¹⁾ present an excellent discussion of ion exchange in oxidised cellulose and discuss the base exchange capacity of oxycellulose in the presence of appreciable reducing capacity. Occasionally, reducing power and ion exchange capacity are confused by certain methods of analysis. Davidson & Nevell examined several methods of determining the carboxyl content and exchange capacity of celluloses and recommend silver metanitrophenolate for this purpose. Determination of the base exchange capacity of cellulose for various ions gave the following order of increasing affinity for cations at 0.01N—



Rath & Dolmetsch⁽²²⁾ also studied the affinities of various cations for cellulose and they, along with Church,⁽²³⁾ claim that cellulose combines with an equal number of cations regardless of their valency rather than binding the same number of equivalents. Combination with an equal number of cations corresponds for polyvalent cations to the formation of a basic salt of a mixed salt such as $\text{R}_{\text{cell}} \text{CaCl}$. Farrar and Neale⁽²⁴⁾ examined cation and anion distribution ratios for several simple salts between cellulose and water. The ionic distribution found was in general agreement with the Donnan theory, if water is considered the solvent in both phases.

Cations of basic dyes are found to undergo exchange with the carboxyl group of cellulose fibres. This phenomenon has been studied in particular by Weber & Huseman,⁽²⁵⁾ who employed a colorimetric method. Davidson⁽²⁶⁾ critically examined Weber & Huseman's method and showed that it is necessary to control the pH value and give ample time for equilibrium in cation exchange reactions. Davidson suggests that methylene blue absorption is the best method for determining carboxyl content of celluloses having low carboxyl contents. Davidson⁽²⁶⁾ also studied the relative affinities of several basic dye cations and found wide differences, but all of them had stronger affinities than sodium ion. The exchange capacity of basic dye cations did not conform to the mass law, but rather to the following equation—

$$R = Kr^p$$

where R and r are the ratios of concentrations of the competing cations in cellulose and the solution phases, respectively, K is a constant and p is a constant less than unity.

The uptake of aluminium ion has also been studied by several workers, notably, Ekwall & Bruun.⁽²⁷⁾ These workers showed that sorption of aluminium ion by cellulose fibres is a function of the number of acid groups on the cellulose and of the pH value. Below pH 3.5, aluminium ion sorption is negligible on all pulps; between pH 3.5 and 5.0, the uptake is a linear function of the pH value. Approximately 40 per cent of the acid groups are exchanged when pH 5.0 is reached; above pH 5, alumina begins to precipitate and deposit, so data were unobtainable. Ninck Blok⁽²⁸⁾ also showed that aluminium ion uptake was directly related to the carboxyl content of the pulp. Aluminium ion adsorption increased with increasing concentration of aluminium salt and followed a Freundlich-type isotherm. A technical pulp picked up more aluminium ion than acid-washed pulp from which the calcium ion had been removed. Ninck Blok explained this difference by the exchange of calcium ion for aluminium ion in the technical pulp. It was suggested that the acid treatment and removal of calcium ion destroys some of the exchange sites.

Launer⁽²⁹⁾ states that pulp fibres often remove 33–45 per cent of aluminium from a furnish containing the normal amount of alum. He also observed that, if the pH value of an alum solution is reduced by heating (this increases the hydrolysis) and, after cooling, woodpulp is immersed in it, the pH value increases. He attributes this to preferential absorption of hydrogen ion, but it is quite possible that calcium ion exchange as noted by Ninck Blok may occur also with technical pulps such as Launer used. Absorption of aluminium complex ions (produced by hydrolysis) may have also affected the pH value in this case.

The recently renewed emphasis upon the relationship between general deterioration of paper and sheet acidity prompted Reynolds & Linke⁽³⁰⁾ to examine the effects of alum and pH value upon extractable acidity. They found that extractable acidity is not a simple function of stock pH value, but is influenced by alum floc retention and change in floc composition consequent on drying conditions and the presence of sulphate ions. The sulphate content of the sheet was related to acidity, but the maximum acidity did not correspond to maximum sulphate retention. The whitewater was not recirculated in these experiments.

White and co-workers⁽³¹⁻³³⁾ studied the absorption of cationic surface-active agents by cellulosic materials. This work includes the determination of the absorption isotherms for both cation and anions of the surface-active agent, rates of absorption and the effects of temperature, added electrolyte and solubilised dyes. They concluded that two major sorption processes occur in the concentration range studied—cation exchange and ion-pair absorption. The cation exchange is dependent on the exchange capacity of the cellulose substrate; the ion-pair absorption begins to be important in the vicinity of the critical micelle concentration of the surface-active agent and seems to depend on the cation exchange capacity of the substrate. The effects of esterification of the carboxyl groups on cation and ion-pair absorptions were also studied. A theoretical model for the absorption process was proposed; it consists of absorption of the cations by an exchange process followed by a clustering of ion pairs on the exchanged cations.

Swanson & Cordingly⁽⁹⁾ have shown that the presence of various ions in pulp affects the rate of development of self-sizing arising from the vapour phase redistribution of the natural resins and fatty materials present in all woodpulp. Multivalent ions are particularly detrimental, divalent salts are undesirable, whereas alkalis decrease the rate of development of sizing to a substantial degree. Sinclair, Evans & Sallans⁽³⁴⁾ used multivalent ions such as lead, copper, iron, chromium, aluminium and zinc to prepare sized papers and board from the natural sizing materials within the pulp. Czepiel⁽⁵²⁾ showed that traces of iron and copper in a cotton pulp will accelerate colour reversion and physical degradation of paper. Manganese salts on the other hand were unexpectedly found to retard the rate at which cellulose discolours.

In summary, the base exchange capacity of cellulose fibres results mainly from carboxyl groups introduced on the chains by oxidation and from the presence of acidic hemicelluloses. Highly purified pulps have low base exchange capacity and can absorb very little aluminium ion and have a low ash content. Generally, they do not show an acidic character in their various reactions. Unpurified pulps, however, are sufficiently acidic in character to undergo various surface reactions that may be related to their base exchange capacity.

Effects of electrolytes on fibre swelling, beating rate and drainage

Cellulose fibres in water comprise a gel whose rate and degree of swelling is affected by the presence of electrolytes. Because swelling of cellulose fibres plays such an important role in drainage and in obtaining molecular contact for good interfibre bonding, it is not surprising that a great deal of attention has been given to these effects. Much of the early literature on the effects of electrolytes is reviewed by Casey.⁽³⁵⁾

General effects—Among the early investigators in this field are Mansfield & Stephenson,⁽³⁶⁾ who showed that hydration and beating rate of sulphite pulps were increased in the presence of certain soluble alkalis and salts. For example, 1 per cent of sodium carbonate increased bursting strength by 69 per cent over similar beating in pure water. Sodium hydroxide, zinc chloride and ammonia gave only slightly lower effects. On the other hand, 5 per cent sulphuric acid and 10 per cent sodium chloride did not influence bursting strength. Alkalis such as sodium hydroxide, soda ash and sodium silicate have long been used in the industry for accelerating the beating rate of pulps and, indeed, continue to be employed for this purpose. It is common practice in many paperboard mills to refine the stock at pH 8.5–10.5 and at a temperature as high as 160°F. Approximately 15 per cent greater strength properties are obtained on many reprocessed papers under these conditions. The higher temperature has the effect of decreasing fibre swelling somewhat, but speeds drainage on the wire. Höpner, Jayme and Ulrich⁽¹³⁸⁾ found that fibre swelling determined by the centrifugal method was unaffected by calcium water hardness 1 000 ppm.

Centola & Borruso^(135, 136) found that beating in the presence of substantive dyes such as Congo Red, Benzopurpin 4B, Chicago Blue 6B and Direct Blue 2B accelerates hydration of the pulp. The effects were more pronounced when the dyes were purified from the usual salts.

The most extensive work on the effects of electrolytes on pulp and paper properties is that of Cohen, Farrant & Watson^(40, 41). The influence of cations on a water-washed pulp varied with their valency and concentration.⁽⁴⁰⁾ Generally speaking, rate of beating and strength properties were enhanced by monovalent cations, retarded and reduced by trivalent and quadrivalent cations, unaffected by divalent cations over the concentration range of 0.001—0.016N. It is interesting that ion antagonism was observed in systems containing a mixture of monovalent and trivalent cations. It was possible to counteract the retarding influence of 50 ppm of trivalent cerous cations by the addition of 200 ppm of sodium chloride.

In contrast to the varied effects on strength, all electrolytes increased the freeness of the stock and sheet air permeability and the effects increased with the valency of the cation. These effects were explained by the changes in

electrokinetic properties of the fibres. See the following section for a discussion of these effects.

Cohen and co-workers⁽⁴¹⁾ also determined the effects of the following anions on an unbleached eucalypt kraft pulp and its paper properties—hexametaphosphate, hydroxide, citrate, bicarbonate, phosphate, acetate, ferrocyanide, nitrate, sulphate and chloride. With the exceptions of sodium hydroxide, which produced a highly significant increase in pH value and of sodium hexametaphosphate, which produced extraordinary effects, all electrolytes influenced drainage and sheet properties in a manner attributed to the action of a monovalent cation. The effects of sodium hexametaphosphate passed through a maximum at a concentration range of 0.001–0.002N and were greater than those produced by other electrolytes. Its dispersive action and ability to sequester the multivalent cations naturally present in the pulp gave improved sheet formation and greater air resistance. The sequestration effects liberated carboxyl groups, which presumably permitted the pulp to swell and imbibe more water and thereby produce better bonding. These workers concluded that water-washed pulps are insensitive to divalent cations, because they already contain these ions in combination with the carboxyl groups.

Adams, Simonds & Baird⁽⁴²⁾ found the Schopper-Riegler freeness of mechanical woodpulp and beaten chemical woodpulp increased to maximum values when very small amounts of non-alkaline electrolytes were added. Alum additions over the range of 0.001–0.052N changed the freeness of a bleached sulphite reference pulp from 550 cm³ to 680 cm³. The pH value ranged 7.28–3.70 and use of sulphuric acid with or without alum gave similar freeness effects. Alkaline electrolytes such as sodium carbonate and sodium hydroxide had little (if any) effect on freeness.

MacGugan⁽⁴³⁾ noted that a number of unbleached kraft mills use calcium chloride for drainage improvement on the wire. Investigation revealed that addition of 0.5–10.0 per cent (pulp basis) of calcium chloride to the refined pulp in soft water changed the Canadian standard freeness from 411 cm³ to 516 cm³. The recommended level is 1.0–1.5 per cent of calcium chloride based on the pulp. Addition of the salt during refining required an increase in refining power to attain the same degree of refining. The effects of calcium chloride are considerably decreased in hard water.

Touchette & Jenness⁽⁸⁴⁾ found that cationic surfactants significantly increased the drainage rate as indicated by Canadian standard freeness. Anionic and non-ionic materials decreased freeness. All types of surfactant, however, were found to facilitate water removal on a sheet mould wire as indicated by the final weight of the wet sheet. The cationic products produced a substantial decrease in bursting and tensile strengths, whereas the effects of

anionic and non-ionic materials were variable, but much smaller. These effects agree with those found in the earlier work of Dixon.⁽⁸⁵⁾

The effects of surfactants on strength properties of pulps have not been worked out in detail, but three factors appear to be involved depending upon the ionic or non-ionic nature of the product—(1) surfactants lower the surface tension of the water to a sufficient extent to decrease the Campbell effect during drying and consolidation of the sheet as shown by Lyne & Gallay;⁽⁷¹⁾ (2) surfactants are adsorbed by the surfaces of fibres and fibrils and the adsorbed films may interfere with normal hydrogen bonding between fibre surfaces; (3) cationic surfactants at low concentrations can flocculate cellulose fibres and thereby give poor bond distribution in the sheet.

Electrokinetic effects—Almost every investigator of the effects of electrolytes on stock drainage behaviour has attempted to explain his results on the basis of possible electrokinetic effects. The relationship between electrolyte concentration and electrokinetic effects on cellulose fibres has been studied by several investigators and is reviewed by Higgins.⁽⁴⁾ There are several articles in which surface electrical properties of fibrous materials are directly related to drainage measurements. Carolane⁽⁴⁴⁾ studied the effects of two cationic additives, alum and chrome glue, on the zeta-potential and drainage rate relationship of pulp fines. When alum was used, the Canadian standard freeness increased up to the isoelectric point (at approximately 100 mg/litre) then remained constant at higher alum levels. With chrome glue, the freeness rose sharply to a maximum as the zeta-potential passed through the isoelectric region and became positive, then the freeness decreased well below the maximum at higher concentrations, in some cases back to the original freeness. It is observed, however, that the maximum freeness occurred at somewhat lower additive concentrations than those corresponding to the isoelectric point. There is also some question about whether the electrokinetic properties of the fines are representative of those of the whole pulp.

Goring & Mason⁽³⁷⁾ measured the electrokinetic properties and hydrodynamic swollen volume of bleached sulphite pulp in dilute electrolytes (2.5×10^{-5} – 2×10^{-2} N potassium chloride and 1.4 – 2.1×10^{-4} N thorium chloride) by the stream compression method. The hydrodynamic specific swollen volume of the fibres was a maximum close to the isoelectric point, but all values were considerably larger than those obtained on the same pulps by the liquid permeability method employing the Kozeny-Carman equation. This discrepancy was later found⁽³⁸⁾ to result from the fact that the pore orientation factor in the pad is proportional to ϵ^3 (the effective void fraction) for electrokinetic movement and to ϵ for ionic conduction, but is constant for permeation. This work also indicated that Briggs' method⁽³⁹⁾ for measure-

ment of zeta-potentials is invalid and that all measurements in the prior literature except those for single circular capillaries are probably in error.

Hästbacka & Nordman⁽⁴⁵⁾ studied the effects of aluminium chloride, thorium chloride and pH value on the zeta-potential and the Schopper-Riegler number of whole unbleached sulphite pulp under corresponding conditions. A minimum zeta-potential (-20 mV) was obtained at an aluminium chloride concentration of about 0.05 milliequivalent/litre, after which the value increased asymptotically toward the zero line. Contrary to the results of Thode & Htoo,⁽⁴⁶⁾ the potential curve did not cross the line and become positive at higher concentrations of aluminium chloride. When the pH value was adjusted to 4.5 at each aluminium chloride concentration, however, an isoelectric point was reached at an aluminium chloride concentration of about 2 milliequivalents/litre; at higher concentrations, the pulp then became positively charged. The maximum effect of aluminium salt on the zeta-potential was obtained when 2.5 equivalents of sodium hydroxide were added per trivalent aluminium ion. When this amount of alkali was exceeded, the potential decreased. The change of zeta-potential from a negative to a positive value was accompanied by a minimum in the Schopper-Riegler number curve indicating a maximum drainage rate at the isoelectric condition. Addition of thorium chloride to the pulp also gave a sharp maximum in drainage rate when the isoelectric point was reached. Adjustment to pH 4.5 sharply reduced the drainage rate on the positive side of the isoelectric point, presumably because of hydrolysis of the thorium chloride. It was observed that adjustments of pulp to pH 4.5 in the presence of sodium chloride and calcium chloride had very slight effects on drainage properties. These investigators also showed that the permeability coefficient (K) calculated from Darcy's law more than doubled in value when the electrical charge on the fibres is eliminated. This effect may be due partially to fibre flocculation. It is interesting that the hydrodynamic specific surface areas of Goring and Mason's pulps⁽³⁷⁾ are at a minimum near the isoelectric point of the fibres. This may indicate a collapse of fibrillar structure or of their proposed diffuse β -layer on the fibre surface under this condition.

Guide,^(47, 48) Thode and co-workers^(46, 49-51) and Ninck Blok⁽²⁸⁾ have studied the effects of various anions and cations on the electrokinetic properties of fibres in connexion with rosin sizing.

Ionic, water-soluble polymers such as polyethylenimine⁽⁷⁵⁾ and high molecular weight polyacrylamides^(76, 77) are also used as drainage aids. Under the conditions employed (very low concentrations), it is probable that these materials improve drainage by flocculation of the fines, if not the longer fibres. Various gums may be used as well to improve drainage by decreasing the refining and maintaining strength properties at a desired level

by addition of a small percentage of the gum.⁽⁶⁹⁾ The mechanism of this action has not been investigated, but may depend upon the principles outlined by La Mer and co-workers.⁽⁷⁸⁻⁸⁰⁾

The effects of additives on fibre flocculation

THE term fibre flocculation refers to the process of aggregation by which localised variations in pulp concentration occur throughout the suspension. The flocs apparently form during the movement of fibres relative to one another, whereupon the shear forces—(1) bring fibres into contact, (2) entangle the fibres and/or permit them to adhere and (3) subsequently redisperse some of the flocs. The first and third processes are purely mechanical and may be related to the type and strength of the shearing forces. The second stage is both mechanical and chemical and may be influenced by chemical means. At a given set of shear conditions, an equilibrium occurs between the rate of formation of fibre flocs and their rate of dispersion. A high degree of fibre flocculation at the time the sheet is formed on the wire is manifested as poor formation and poor fibre bond distribution in the final paper.

The order of magnitude of the effect of formation on the strength of paper may be obtained from the work of Leech.⁽²⁾ He prepared papers of various formation numbers from the same beaten pulp by variation of pulp consistency and flocculation time before the sheets were made. An increase of 20 points (from 21.9 to 42.0) in Thwing formation number⁽⁵³⁾ gave a 40 per cent increase (60 to 84 points per 100 lb) in bursting strength and a 24 per cent increase in tensile strength. Tear factor was less sensitive to fibre distribution—an 8 per cent increase was noted with the improved formation.

Flocculation of both fibres and fines also has marked effects upon the consistency at which pulps may be pumped, upon riffling operations, screening and dirt removal, drainage on the wire, retention of fines and fillers, many structural and surface properties of the paper and the efficiency of recovery of whitewater.

Numerous factors affect the degree of fibre flocculation such as the type of pulp, fibre length, temperature and viscosity of the water, the type of beating, fibre consistency, the mechanical shear conditions of forming the sheet, the presence of ions (particularly multivalent ions), the presence of flocculating materials such as alumina and pigments, the presence of gums and other natural and synthetic polymers. The mechanism of fibre flocculation and the effects of mechanical and structural factors have been studied by Wollwage,⁽⁵⁵⁾ Erspamer,⁽⁶⁴⁾ Mason,⁽⁶¹⁾ Hubley, Robertson & Mason⁽⁵⁷⁾ and reviewed by Higgins.⁽⁴⁾ It is generally agreed that longer fibre length, greater fibre flexibility and higher consistency increase flocculation, but there appears to be

considerable disagreement about the effects of many colloidal factors upon fibre flocculation. Perhaps this disagreement stems from the widely different methods and conditions employed for study.

Measurement of fibre flocculation

A variety of methods has been used for the study of fibre flocculation and include such simple techniques as measurement of the time for discernible flocs to appear in dilute (0.1 per cent) dispersed pulp suspension held in a large cylinder,⁽⁵⁴⁾ time of flocculation of a dispersed stock passing through a cylindrical tube,^(55, 66) optical measurement of equilibrium condition of sheared dilute stock suspension,^(56, 57) direct tensile strength measurement of fibre flocs at papermaking concentration,⁽⁵⁸⁾ measurement of the uniformity of stationary fibre suspensions,^(59, 60) measurement of equilibrium of state of flocculation in turbulently flowing suspension⁽⁶¹⁻⁶³⁾ and the formation of standard handsheets.^(64, 65) Several of these methods have been used for study of the effects of non-fibrous additives on fibre flocculation.

Effects of salts

Generally speaking, the effects of salts on fibre flocculation follow their colloidal effects on electrokinetic charge and coagulation. Wollwage,⁽⁵⁵⁾ working with unbleached sulphite pulp at a consistency of 0.01 per cent, found that tap water and alum at first flocculated the fibres, but, after thorough mixing, alum improved dispersion to a marked degree. Under similar conditions in distilled water, alum produced only slightly better fibre dispersion until sodium hydroxide was added, whereupon marked fibre dispersion was obtained. He suggested that alumina was necessary for best fibre dispersion. Similar results were obtained by Erspamer,⁽⁶⁴⁾ de Roos,⁽⁶²⁾ Beasley,⁽⁶⁶⁾ Andersson & Brunsvick⁽⁶⁷⁾ and Jacquelin.⁽⁶³⁾ Divalent and monovalent ions were less effective than aluminium ion. Tetrasodium pyrophosphate was found by Erspamer⁽⁶⁴⁾ to give improved fibre dispersion comparable to alum when used in tap water, but no effect could be obtained in distilled water. Beasley⁽⁶⁶⁾ found no beneficial effect with sodium hexametaphosphate. The effects of change in pH value alone are negligible.^(55, 66, 67) All of these studies were carried out at low fibre consistencies and low rates of shear. On the other hand, Hubley, Robertson & Mason⁽⁵⁷⁾ working at somewhat higher consistencies (0.02-0.05 per cent) found that addition of electrolytes such as alum and thorium chloride in quantities sufficient to lower and reverse the sign of the zeta-potential have a negligible effect on fibre flocculation over the range of shear rates studied, 12-70 sec⁻¹. The shear rate of Wollwage's method was of the order of one reciprocal second, whereas that of Erspamer was close to zero.

The works of Erspamer,⁽⁶⁴⁾ Wollwage⁽⁵⁵⁾ and Beasley⁽⁶⁶⁾ clearly show that ionic effects alter the flocculation rates of fibres under conditions of low consistency and low shear rate. The evidence of Hubley, Robertson & Mason⁽⁵⁷⁾ indicates, however, that ionic effects are appreciable only at very low rates of shear and low consistencies. Papermakers have claimed for years that alum improves formation on the wire, but alum is employed as well for improving retention of fines and fillers. It appears as though further work must be done at higher consistencies typical of the papermaking operation before an adequate understanding of these phenomena is to be had.

Effects of surface-active agents

The effects of surface-active agents on fibre flocculation have been studied by several investigators. Wollwage⁽⁵⁵⁾ observed a small increase in flocculation with 15 per cent of a sulphonated alcohol-type wetting agent based on the fibre. This was sufficient wetting agent to lower the surface tension of water from 72 to 51 dyne/cm². Erspamer⁽⁶⁴⁾ found that anionic wetting agents (sodium lauryl sulphate and Turkey red oil) in the presence of alum and air, flocculated pulp fibres and caused them to float, but addition of cationically charged products (Du Pont Product BC and Onyxsan S) to alum-dispersed pulp enhanced the dispersion. Increasing amounts of Onyxsan S to pulp alone caused marked flocculation at low concentrations, but caused dispersion of fibres at higher concentration. Thode and co-workers⁽⁷⁰⁾ obtained fibre dispersion with anionic and non-ionic wetting agents, but Beasley⁽⁶⁶⁾ obtained no measurable effect with anionic, cationic or nonionic surface-active agents. This may have been caused by the low fibre consistency employed: see the following discussion of this effect.

In summary, ionic effects on fibre flocculation are discernible at low fibre consistencies, but are of lesser importance in the consistency range more typical of papermaking operations.

Hydrophilic polymers as fibre deflocculants

There are certain natural and synthetic water-dispersible polymers that have a much more pronounced effect upon fibre flocculation than have electrolytes of low molecular weight. These additives, some of which are polyelectrolytes and others neutral polymers, are in a class by themselves for their effectiveness. Among these materials are the mannogalactan gums from locust beans (*Ceratonia siliqua*) and guar (*Cyamopsis tetragonoloba*), deacetylated karaya gum (*Sterculia urens*), carboxymethyl cellulose^(54, 65) and the mucilages from alginic acid,^(54, 65) *Hibiscus manihot* root⁽⁷³⁾ and okra pod (*H. esculentus*). The use of these materials as fibre deflocculants has been studied by Harrison,⁽⁶⁸⁾ Swanson,⁽⁶⁹⁾ Andersson & Brunsvick,⁽⁶⁷⁾ de Roos⁽⁶²⁾

Mason and co-workers,^(57, 61) Jacquelin⁽⁶³⁾ and Shogenji & Takahashi.^(54, 65) The effects on fibre flocculation are striking not only at papermaking consistencies, but may be observed also as a reduction of pipe friction at pulp concentrations at which stock may be pumped around the mill—see Gray & Van den Akker⁽⁷²⁾ and Forgacs, Robertson & Mason.⁽⁵⁸⁾

All investigators agree about the superior effects of such deflocculants in concentrations above 0.5 per cent based on the fibre, although Mason and co-workers^(57, 61) have observed that these materials have a pronounced *flocculating* (instead of dispersing) effect on fibre fines. Jacquelin's⁽⁶³⁾ figures show that mannogalactan gums have a flocculating effect even on whole pulps at concentrations below 0.5 per cent and this is particularly evident at higher degrees of beating, which may indicate that specific surface is important. As a matter of fact, papermakers take advantage of the coagulating effect of vegetable gums on fines to improve retention.⁽⁷⁴⁾

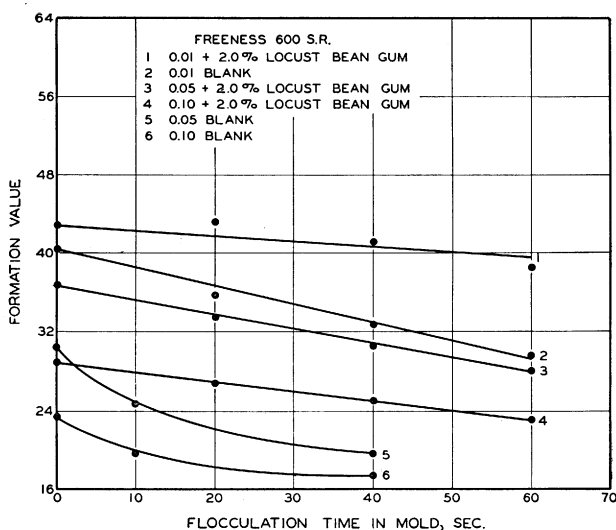


Fig. 1—The effect of consistency and locust bean gum on flocculation of a bleached sulphite pulp

Some years ago, when the development of guar gum was under way,⁽¹³⁷⁾ considerable differences were noted between the fibre deflocculation efficiency of gum products that had been processed under slightly different conditions. Testing of these materials in Wollwage's apparatus revealed no difference in effectiveness, whereas marked differences occurred on the papermachine. These observations led to an investigation of Erspamer's method for evaluating vegetable gums and this technique permitted clear distinction between

the gums in the same order of effectiveness as shown on the machine. An investigation of the effects of consistency on fibre flocculation was made as shown by the data in Fig. 1. The curves indicate that the vegetable gums under the conditions of these techniques simply slow the rate of fibre flocculation—at a fibre consistency of 0.01 per cent, typical of the Wollwage method, flocculation was so slow that no distinction could be made between good and poor quality fibre deflocculants at short flocculation times. At higher consistencies, typical of the Erspamer method (0.055 per cent), flocculation was sufficiently rapid that good distinction could be obtained. In addition, it was possible to obtain estimates of the relative effectiveness of such gums in the presence of alum as shown in Fig. 2.

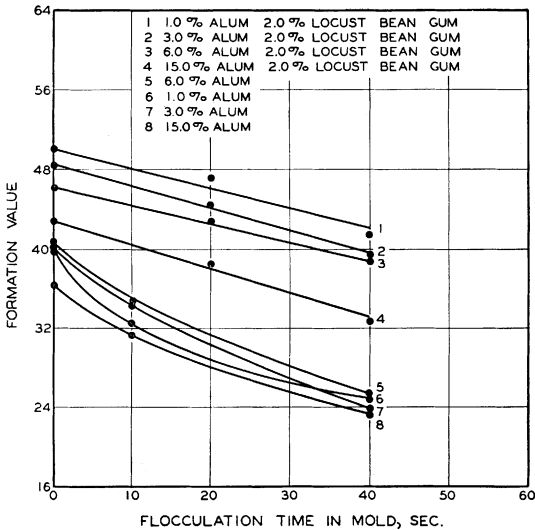


Fig. 2—The effect of rosin, alum and locust bean gum on the formation values of sulphite pulp handsheets made at various flocculation times (rosin 2 per cent, pulp consistency 0.03 per cent)

The mechanism of improvement of fibre dispersion in the presence of hydrophilic polymers has not yet been worked out. Wollwage⁽⁵⁵⁾ suggested that the increase of viscosity of the water was partly responsible, for he had found that higher viscosity of water obtained by lower temperature or addition of glycerine improved fibre flocculation. Erspamer⁽⁶⁴⁾ suggested that a combination electrokinetic and protective colloid effect is responsible.

The electrokinetic effect must be very small with the mannogalactan gums, because both the fibre and gum have low potentials under the conditions of use. Mason and co-workers⁽⁵⁸⁾ have proposed several other possibilities—(1) that the polymers have a lubricating effect upon the fibre surface; (2) that the mechanical properties of the highly swollen sorbed material may reduce the frictional resistance between fibre surfaces in addition to any charge effect that may be present; (3) that the highly swollen material consists of large micelles that cause coagulation of fines as a result of entanglement or attractive forces and (4) that the presence of the discrete particles between fibres inhibits fibre contacts and improves formation and sheet bulk in a manner similar to added diatomaceous earth. These suggestions are in agreement with the pituitous or stringy quality required of the best polymer deflocculants used for papers made from manila pulp or synthetic fibres.

When the uronide polysaccharides such as deacetylated karaya gum, *H. manihot* extract, okra, sodium alginate and carboxymethylcellulose are used in commercial practice, multivalent ions such as water hardness and particularly alum must be carefully avoided, otherwise pronounced clotting of the pulp occurs and formation of the paper is worse than if no deflocculant were used. This effect is believed to be caused by an ionic cross-linking of the polymer-fibre complex through a chemical reaction with the ionised carboxyl groups.

The observation by Hubley and co-workers⁽⁵⁷⁾ that the same concentration of fibre deflocculant will disperse long fibres and simultaneously coagulate the fines may be explained by means of the polymer flocculation theory of Smellie & La Mer⁽⁷⁸⁾ and Healy & La Mer.^(79, 80) These workers point out that chemical interactions that operate in polymer flocculation are very intense at short range and are sufficient in magnitude in many instances to overwhelm electrostatic repulsion between particles having net charges of the same sign. They suggest that, at low polymer concentrations, one end of the polymer chain (which is attached at its other end to a solid particle) now attaches itself to uncovered surface on a second particle, producing a network that leads to flocculation. Using a modified Smoluchowski coagulation equation, it is postulated that the probability of building flocs is proportional to the fraction of the surface covered by polymer (θ) and to the fraction of the surface that is uncovered ($1 - \theta$). The rate of floc formation $-dn_0/dt$, expressed as the decrease in the number of primary particles n_0 , will depend upon the product $\theta(1 - \theta)$ and is given by—

$$-dn_0/dt = k_1 n_0^2 \theta(1 - \theta)$$

where the number of floc nuclei and the number of particles per unit volume available to add to the floc nuclei are both proportional to n_0^2 . Thus, the

bridging mechanism involves a bimolecular process, where $n_0\theta$ represents the concentration of active species containing flocculant and $n_0(1-\theta)$ represents the concentration of species with open surface able to react with the first species. Smellie & La Mer⁽⁷⁸⁾ observed that their systems first flocculated, then, with either increased time of agitation or with increased polymer concentration, the system redisperses. This is precisely the behaviour of the pulp/deflocculant system at low polymer concentrations. Since the fines have a much higher specific surface than the fibres, they may be expected to flocculate at a polymer concentration that normally causes dispersion of the longer fibres. Another interesting point about La Mer's work is that the flocculated system undergoes much more rapid filtration than the dispersed system. A further investigation of this concept as applied to fibre flocculation is warranted.

Effects of wet strength resins

THE manufacture of wet strength paper and paperboard products by the wet end addition of water soluble polyelectrolytes is one of the important technical achievements of the industry during the last 25 years. In spite of its importance and the rather considerable study given to these polymers, neither the mechanism of their retention nor the mechanism of the development of wet strength in paper is well understood. The following remarks will be directed to several recent studies of these two problems.

Mechanism of retention of wet strength polymers

In order for a polymer to function as an adhesive in a rigid structure, adsorption of molecules must occur on to the solid surfaces to be bonded. Thermodynamic theory requires that spontaneous adsorption of the polymer from solution must involve a reduction of the total free energy of the system. This may be summarised in terms of the first and second laws—

$$\Delta H = \Delta F + T\Delta S$$

where ΔF is the change in free energy of the system, ΔH is the heat of adsorption or enthalpy of the process, T is the absolute temperature and ΔS is the change in entropy of the system.

Experimentally determined enthalpy values for polymer/solid adsorption of several systems⁽⁸¹⁾ have given both negative and positive small values of the order of a few thousand calories per mole. It should be remembered that the enthalpy is comprised of several quantities—the enthalpy of polymer segments, the effect of solvent adsorption and the enthalpy associated with extended segments of polymer. Similarly, the change in entropy is made up of the entropy contributions from attached and extended polymer segments

and adsorbed and free solvent molecules. If ΔH is positive and the total free energy change must be negative for a spontaneous process, ΔS is positive and larger than $\Delta H/T$. The entropy change accompanying adsorption of polymer is a loss of entropy, so the entropy released to the system by solvent molecules displaced from the surface must be the driving force that controls the free energy of adsorption.⁽⁸⁰⁾ It is not a simple matter therefore to predict from the chemistry of a system whether or not a polymer will prefer to fix itself spontaneously upon the fibre surface. It would appear that the most that can be said at present is that neither the polymer nor the sorption site on the solid surface should be highly solvated. This means that the aqueous phase should not be a good solvent for the polymer in the usual thermodynamic sense. Because these solvation effects are difficult to determine for poly-electrolyte systems, further information can at present be obtained only by indirect means. More elaborate discussions of these concepts are given for synthetic polymer systems by Simha, Frisch & Eirich,^(82, 83) Higuchi⁽⁸⁶⁾ and Silberberg.⁽⁸⁷⁾ No work of this kind has been done for wet strength resins.

The most widely used wet strength polymers ionise as polycations in aqueous solution and it is commonly believed that retention occurs by electrostatic interaction of positively charged polymer with the negatively charged fibre surface. Actually, many polymers that have the same sign in electrokinetic potential as the fibre surface are rapidly adsorbed from very dilute solution—for example, the mannogalactan gums. Thus, the retention process is much more complex and deserves much more study. It appears as though a difference in sign of electrokinetic charge between the polymer and solid surface serves only to accelerate the kinetics of getting the polymer to the surface so that the adsorption process can occur. Consider, for example, the retention of a cationically stabilised latex by negatively charged pulp fibres. Upon mixing the latex with the pulp, rapid coagulation upon the fibre appears to occur and the interfibre water may become optically clear, if only a modest amount of latex is added. When paper is formed from such treated stock in the usual way, however, retention of this cationic polymer is no greater than that of an anionically charged polymer that has been flocculated with alum. The point here is that the hydraulic forces on the wire are sufficient to remove a large part of the polymer from the sheet in both cases, because the electrical forces are inadequate. This lower retention does not occur, if the deposited polymer becomes adsorbed after contacting the surface. As a matter of fact, many adsorbed polymers are held so strongly that the macromolecule must be destroyed before it can be removed. It is presumed that many of the polysaccharide and wet strength polymers are adsorbed through a hydrogen bonding mechanism. Even though the hydrogen bond involves an energy of 5–10 kcal/mole, many such bonds may form

between the surface and the repeating units of a single macromolecule. Thus, the strength of bonding may approximate that of primary valency bonds, because statistically it is unlikely that all such hydrogen bonds would be broken simultaneously.

The works of Steenberg⁽⁸⁸⁾ and Kennedy⁽⁸⁹⁾ on urea-formaldehyde resins and Wilfinger⁽⁷⁵⁾ and Sarkanen and co-workers on polyethylenimine⁽⁹⁰⁾ support the theory that many cationic wet strength resins are retained on fibres by an ion exchange mechanism. In these cases, there is a very good correlation between the carboxyl content of the pulp and retention. The role of carboxyl content in retention should not be confused with electrical charge effects as measured by zeta-potential. Contrary to what many people believe, the electrokinetic potential of cellulose fibres decreases regularly with increasing carboxyl content.^(91, 52)

Properly prepared melamine-formaldehyde resin acid colloid⁽⁹²⁾ or cationic urea-formaldehyde polymers are adsorbed upon cellulose fibres at normal papermaking consistencies extremely rapidly, that is, in a matter of seconds.^(93, 88, 94) Henrickson & Steenberg⁽⁹⁴⁾ commented that adsorption of urea-formaldehyde was so rapid that it was impossible to study the rate process in detail. They made the further observation that part of the resin was not as rapidly sorbed upon the fibre and this fraction was not effective in producing wet strength. Landes & Maxwell⁽⁹²⁾ and Dixon, Christopher & Salley⁽⁹⁵⁾ show for melamine resins that higher molecular weights are beneficial to retention.

Anions have an important effect upon retention of wet strength resins. Maxwell & Reynolds⁽⁹⁶⁾ found the chloride ion to have a small effect, but sulphate and ferricyanide ions showed much more pronounced effects. For example, the sulphate ion initially increased wet strength efficiency (presumably improved retention) up to 75 ppm of sulphate, but this was followed by a rapid loss in wet strength at higher concentrations. A similar, but more pronounced effect occurred with the ferricyanide ion. High efficiency (HE) melamine resins prepared with larger ratios of formaldehyde to melamine are less sensitive to sulphate ion, but are less well retained, because of greater solvation effects.⁽⁹⁷⁾

The above literature indicates that numerous factors influence rate and extent of retention of wet strength resins by papermaking fibres. Thode, Swanson, Kurath & Hoffman⁽⁹⁸⁾ obtained a further insight into the mechanism of retention through a kinetic and thermodynamic study. The rate of adsorption of melamine acid colloid was successfully followed at various temperatures, pH values and fibre surface areas at a very low fibre consistency (0.01 per cent). A modified cationic urea-formaldehyde resin was examined similarly.⁽⁹⁹⁾ Fibre fines and foreign electrolytes were avoided and sufficient

data were obtained to compute an activation energy for the interaction with a beaten western coniferous sulphite pulp.

The typical data in Fig. 3 show that both the initial rate of sorption and the total amount of polymer sorbed after a long time are directly related to temperature of sorption. It was impossible, however, to determine the relative positions of the curves at equilibrium. If physical adsorption were involved, it might be expected that the curves at higher temperatures should cross those at lower temperatures and longer contact times. Testing of the raw adsorption data indicated that most isotherms obeyed a kinetic first-order

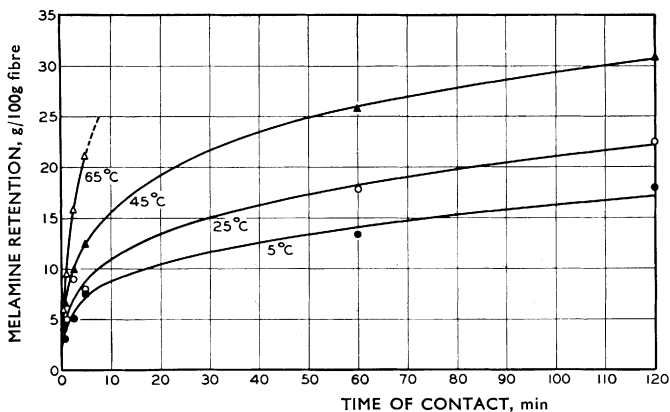


Fig. 3—Melamine retention on beaten sulphite pulp at various temperatures as a function of time (consistency 0.01 per cent, melamine added, 5.0 g/100 g fibre, pH 7.0)

plot in the region of 30–300 sec. Rate constants were plotted against the absolute temperature, according to the integrated form of the Arrhenius equation. The resultant straight line gave activation energies of 5 600 cal/mole for the melamine resin and 5 200 cal/mole for the cationic urea-formaldehyde resin.⁽⁹⁹⁾ These figures may be compared with a value of 14 000 cal/mole obtained for certain dyestuffs⁽¹⁰⁰⁾ and with 4 400 cal/mole for a sorption of a modified locust bean gum.⁽¹⁰¹⁾ These comparisons indicate that sorption of the wet strength resins occurs with ease and a physical process is primarily the rate-controlling step, but a hydrogen bonding mechanism during adsorption may also be indicated, since hydrogen bond energies lie in the range of 4 000–7 000 cal/mole. The rate of transport of polyelectrolyte molecules toward the fibre surface was expressed⁽⁹⁹⁾ by the following equation—

$$j = - \frac{R_s}{\beta} \frac{\partial U(x,t)}{\partial x} - D \frac{\partial R_s}{\partial x}$$

where j is the diffusion current in the x direction in g/sec/cm², D is the diffusion coefficient, β is a friction coefficient, $U(x, t)$ is the potential field about the fibre due to its charge and R_s is the concentration of resin in solution.

In a later discussion of this equation, Thode⁽¹⁰²⁾ proposed on the basis of Neale's⁽¹⁰³⁾ consideration of Donnan approximations for the electrical potential about the fibre that the diffusional transport step is an important rate-controlling step in the entire interaction between fibre and wet strength polymer. Becher, Hoffman & Swanson⁽¹⁰⁴⁾ attempted to determine by study of the role of diffusion, if the surface reaction (bond formation) is rate-controlling or approximately equal in rate to the transport step. To do this, the adsorptions of melamine- and urea-formaldehyde resins were measured as a function of the degree of agitation of the fibre/resin slurry at several resin concentrations. The results showed that resin contents of the fibres increased with increasing rate of agitation up to 1 000 rev/min approximately, indicating that diffusion is the rate-controlling step in the retention process. A diffusion coefficient of 4.5×10^{-6} cm²/sec was obtained by electrophoresis diffusion for the urea-formaldehyde resin, but this increased with time and somewhat with concentration. From a practical standpoint, the results indicate the importance of adding wet strength resins to the stock at a point of adequate, but not severe agitation.

Microscopic examination of fibres stained after treatment with melamine and colloid showed that up to 5 per cent resin is deposited as a uniform film with little or no penetration into the fibre wall, but the resin appeared to penetrate the wall as far as the lumen at much higher concentrations.

Mechanism of wet strength development in paper

The data presented by Britt⁽¹⁰⁵⁾ on the effect of various solvents on the strength of paper point the direction one should seek for the mechanism of development of wet strength. It is shown that the strength of paper varies inversely with the swelling power of the liquid. It is to be expected therefore that water, which promotes fibre bonding, also destroys fibre bonding to an extent dependent upon its ability to swell cellulose in the fibre bond region. The function of a wet strength polymer is to prevent or delay fibre swelling during the functional life of the paper product. Steenberg⁽⁸⁸⁾ suggested that wet strength resins decrease hygroscopicity of the fibres. This mechanism could involve either a physical restraint on the bond region or the formation of chemical cross-links with cellulose.

Jurecic and co-workers⁽¹⁰⁶⁾ impregnated various webs with urea-formaldehyde resin and determined the activation energies for the resin cure during heating. The cellulose papers (unbleached kraft, cotton, cotton linters) had an average activation energy of 22.6 ± 0.8 kg cal/mole compared with $23.8 \pm$

0.6 kg cal/mole for the glass fibre structure. These values are in good agreement and indicate that the reaction leading to wet strength is independent of the type of fibre. The values of the activation energy do not rule out covalent linkages between fibres and resin, if the reactions have equal or lower activation energies to that of the curing reaction.

Attempts were made^(106,107) to determine if chemical bonds were formed by reacting a non-polymerisable model compound 1,1-dimethyl-3-methylol urea with cellulose and with alpha-methylglucoside and the latter with urea-formaldehyde resin. Filter paper treated and subjected to curing conditions (pH 5.0, 4 h at 140°C) did not develop wet strength and more than 95 per cent of the compound could be extracted by water or dilute caustic. This indicates that little if any of the compound formed chemical bonds with the fibre. Heating alpha-methylglucoside with either the urea-formaldehyde resin or the model compound did not change the optical rotation of the mixture. When the glucoside was heated with the resin in an open tube so that water of condensation could escape, the glucoside could be quantitatively recovered by extraction of the cross-linked resin with water. This experiment strongly suggests that chemical bond formation does not occur between the cellulose hydroxyl groups and the wet strength resin. It probably does not preclude reactions between minor components of pulps such as carboxyl and aldehyde groups.

The question that must be resolved is why do papers containing the same amount of resin show widely different wet strength values? Steenberg⁽⁸⁸⁾ and Fineman⁽¹⁰⁸⁾ suggest that the resin diffuses into the more accessible parts of fibres to some degree and restricts swelling or wetting. The wet strength thereby arises from protection of normal fibre bonds rather than from resin-fibre bonds. Fineman's work⁽¹⁰⁸⁾ with starch and hemicelluloses supports this idea.

Jurecic and co-workers⁽¹⁰⁷⁾ argue that partial diffusion of resin into the fibres should lead to stronger resin-fibre anchoring. The actual wet strength is then due to the cross-linking and water insolubility of the resin, partly in and partly outside the cell walls. Curing under these conditions would be kinetically the same as the cross-linking of the resin itself, which is the only reaction that can occur with glass fibres. Curing of the various resin-impregnated papers at 120°C did not increase the dry tensile strength of the kraft paper, but did increase the dry strength of cotton and filter papers. Since dry strength did not increase, no significant number of effective resin-to-fibre bonds exist in kraft paper, though some resin-to-fibre bonds appear to be formed in filter paper.

Effects of gases in paper stock

AERATION of paper stock is a very common phenomenon around the

papermill and the resultant dissolved and dispersed gases pose an increasingly important problem in modern papermaking. When significant quantities of air exist in the stock, severe limitations may occur in stock washer efficiency,⁽¹⁰⁹⁾ pumping capacity, consistency regulation and drainage rate on the wire.⁽¹¹⁰⁻¹¹²⁾

General remarks about foam in the stock system

In addition, foam may cause excessive stock losses, poor basis weight control and formation, reduction in sizing and increased pitch troubles in the stock system and on the papermachine.

The desire for increased production has placed greater demands upon both old and new stock handling equipment, which was in many cases not designed to minimise incorporation of air. Aeration troubles are sometimes augmented by pulping and bleaching residues (from inadequate washing) and by the wide variety of non-fibrous additives used to increase the versatility of paper products. In other instances, water supplies have become contaminated with synthetic detergents that are difficult to remove with ordinary methods of water treatment. These materials may act as foam stabilisers.

An appreciable quantity of foam may develop from the dissolved and chemically combined gases as the colder, saturated water gradually warms up in the mill. Gavelin⁽¹¹³⁾ shows that acidification of water containing 100 ppm of bicarbonate hardness will liberate 40 gal carbon dioxide per 1 000 gal water at atmospheric pressure and 100°F. Thus, if 800 gal fresh water are added to the whitewater system each minute, 32 gal carbon dioxide and 25 gal dissolved air must escape as the temperature is raised. It is not uncommon for kraft stock in a large chest to contain 10 per cent of air by volume.⁽¹¹¹⁾ This is sufficient to cause floating and separation of stock, with consequent poor circulation and significant loss in pulp strength. Generally, however, smaller quantities of gases occur in the stock as it approaches the machine—for example, 0.1–3 per cent by volume.

Perhaps the most difficult troubles with gases occur on the papermachine itself. Occasionally, foaming may be so bad as to remove stock from the head box or vats, but more frequently the bubbles are finely divided and invisible within the stock. The fine bubbles are more difficult to eliminate and they cause fibre flocculation,⁽¹¹³⁾ slower drainage on the wire, throwing of the stock from dandy rolls, pinholes and many other sheet defects. It is clear, however, that dissolved gases are not troublesome so long as they remain dissolved. Drainage measurements in the laboratory are unaffected by the dissolved gases of tap water up to pressure drops of 90 cm of water,⁽¹¹⁴⁾ but drainage on the machine wire may be influenced by gases coming out of solution, because of higher temperatures and the reduced pressure developed

by the leading nips of the table rolls. At very fast machine speeds, Taylor⁽¹¹⁵⁾ has shown that the pressure may be reduced to that of the vapour pressure of water.

Nature of foam

Thermodynamically, foams are unstable and it is useful to consider the process of foaming or frothing as a competition between two rate processes, namely, the rate of foam formation and the rate of collapse of the foam. The collapse of bubbles is delayed by a film-like membrane that resists mechanical rupture and coalescence with neighbouring bubbles. It is well established that a *pure* liquid/gas system does not accumulate foam, because no stabilising film can exist. A third substance capable of being adsorbed at the gas/liquid interface may, however, furnish a protective film around each bubble. Such films may arise in either of two ways—(1) adsorption of surface-active agents and (2) by the concentration of finely divided solid particles around each bubble.

Surface-active agents exist in abundance in most stock systems as the salts of rosin and fatty acids from the pulp. Others may occur in the supply water, depending upon the number of communities and papermills upstream. As a result, all pulps contain surface-active substances. This can easily be demonstrated by allowing a piece of pulp to touch the surface of organically *clean* water that has been dusted with a small amount of ignited talc. A film of the surface-active material is seen to spread rapidly and push the talc particles before it. The chemical composition of several such films has been examined by Langmuir's technique⁽¹¹⁷⁾ and found to consist mainly of ether-soluble pitch, with some lignin and carbohydrate materials.⁽¹¹⁸⁾ It is interesting to note that Green & Leaf⁽¹¹⁹⁾ found that the fractionated foam obtained from a hot water extract of jack pine groundwood pulp contained 44 per cent of pitch and 36 per cent of lignin. They found that the grinder pit whitewater contained 120 mg pitch, 40 mg lignin and 600 mg carbohydrate per litre.

The second means of stabilising foams (by finely divided solid) is also abundantly present in the papermaking system in the form of clays and other pigments, fibre fines, dyes, resinous and lignin components, alumina floc and various sizing materials. Under normal operating conditions, these materials alone do not stabilise foam sufficiently to cause unusual accumulation, unless other surfactants are present or excessive aeration occurs. It is important therefore to eliminate aeration as far as possible at leaky pumps, jordan inlets and outlets, mixing boxes, etc. Installation of mechanical gas removal devices such as water sprays, the Vorvac⁽¹²⁰⁻¹²²⁾ and the Deculator⁽¹²³⁾ or sonic and ultrasonic defoamers⁽¹²⁴⁾ may be desirable.

When a stabilising film is present and foam has a significant time of existence, the protective layer surrounding each bubble drains, becomes thinner, more fragile, more susceptible to mechanical rupture. The surface properties of certain foam stabilisers have marked effects upon these properties and therefore upon the accumulation of foam. Among these properties is the Gibbs-Marangoni effect, which is concerned with the surface elasticity. If a bubble is subjected to mechanical deformation, in general, an increase in surface area results and the surface tension of the new surface is momentarily higher than that of the older surrounding film. The greater surface tension resists further deformation and tries to repair any local damage. Under these conditions, the bubble has greater stability. If, however, the concentration of foam stabiliser in the aqueous phase exceeds its critical micelle concentration, the new bubble surface too quickly attains the original surface tension by adsorption and the mechanical repairing force is smaller and less effective. This may be the reason sometimes that poorly washed pulps do not foam as much as pulps that receive somewhat more complete washing. The surface viscosity of the foam stabiliser is important, too, because it governs the rate at which the foam drains and becomes more fragile. The rheological properties of the surface films can be changed chemically to a less favourable condition, if the chemical nature of the foam stabiliser is known.⁽¹²⁵⁾ Much more work is needed on the pulp/foam system before an adequate understanding is obtained.

Theory of anti-foam action

When the papermaker has eliminated aeration of the stock to the best of his ability, he may add anti-foam chemicals or foam killers to the system. These materials are generally comprised of hydrocarbons, higher alcohols, complex mixtures of fatty acids and glycerides, silicones or polyamides and are at present often used on a basis of trial and error. A useful theory of anti-foam action was developed for several selected foaming systems by Robinson & Wood⁽¹²⁶⁾ and Ross⁽¹²⁷⁾ some years ago and it has been used in a limited way with some success on papermaking systems. The theory is based on observations that rupture of bubbles occurs at speeds of 20–50 mph and that certain glycerides and fatty acids spread at interfaces at about the same speed. Robinson & Wood⁽¹²⁶⁾ observed that anti-foams spread on the surface of the liquid film before rupture of the bubbles occurs. They suggested that spreading of a droplet of anti-foam could be considered equivalent to a rupture in the stabilising film. Under suitable conditions, droplets of anti-foam are drawn by surface tension forces into the liquid film between bubbles, if—

$$\gamma_F + \gamma_{D'F'} > \gamma_D$$

where γ_F is the surface tension of the foaming liquid, γ_D that of the anti-foam agent and the prime marks designate a condition wherein each liquid is saturated with the other.

An entering coefficient E is defined as—

$$E = \gamma_F + \gamma_{D'F'} - \gamma_D \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and, where $E > 0$, the anti-foam is drawn into the liquid film and bridges between two air bubbles. When $E < 0$, the anti-foam is ejected from the liquid film.

Following Harkins' idea of spreading coefficients,⁽¹²⁵⁾ three entering coefficients may be defined—

$$E_{DF} = \gamma_F + \gamma_{D'F'} - \gamma_D \quad . \quad . \quad . \quad . \quad (2)$$

$$E_{D'F} = \gamma_F + \gamma_{D'F'} - \gamma_{D'} \quad . \quad . \quad . \quad . \quad (3)$$

$$E_{D'F'} = \gamma_{F'} + \gamma_{D'F'} - \gamma_{D'} \quad . \quad . \quad . \quad . \quad (4)$$

The initial entering coefficient, equation (2), exists when the anti-foam is first added to the foaming system and the semi-initial coefficient, equation (3), exists when the drops of anti-foam have become saturated with the foaming liquid. Usually, the numerical values of the initial and semi-initial coefficients do not differ much from one another. The final coefficient exists when both phases are mutually saturated.

The anti-foam will spread on the foaming liquid (inside the bubble), if—

$$\gamma_F > \gamma_{D'F'} + \gamma_D \quad . \quad . \quad . \quad . \quad (5)$$

The Harkins' spreading coefficients S_{DF} for the system are—

$$S_{DF} = \gamma_F - \gamma_{D'F'} - \gamma_D \quad . \quad . \quad . \quad . \quad (6)$$

$$S_{D'F} = \gamma_F - \gamma_{D'F'} - \gamma_{D'} \quad . \quad . \quad . \quad . \quad (7)$$

$$S_{D'F'} = \gamma_{F'} - \gamma_{D'F'} - \gamma_{D'} \quad . \quad . \quad . \quad . \quad (8)$$

When the spreading coefficients are positive, the anti-foam will spread as a *duplex film* upon the foaming liquid. According to Ewers & Sutherland,⁽¹²⁹⁾ spreading occurs from this region of higher surface pressure with such speed that it carries with it a layer 10^{-3} cm deep, which thins the bubble film to the critical dimension of 50–100 Å at which easy rupture occurs. Generally speaking, the faster the spreading process, the better is the anti-foam.

It is possible for E to be positive and S to be negative with pairs of liquids having high interfacial tensions, whereas, with pairs of liquids having low interfacial tensions, E and S may be approximately equal. The final spreading coefficient $S_{D'F'}$ is always negative. Therefore, if two liquids F and D become mutually saturated, the liquid D does not enter the liquid F at all or, having entered, it will not spread as a duplex film. This predicts that a good anti-foam must eventually lose much of its anti-foam effectiveness in a reasonably

well-closed whitewater system. This is often found to be true. The effectiveness of an anti-foam may depend equally upon whether the critical micelle concentration of the foaming agent is exceeded.⁽¹³⁰⁾ If this occurs, the anti-foam may be solubilised and become ineffective, unless added in amounts that exceed the solubilisation limit.

Anti-foams, particularly those of the fatty type, should always be prepared with softened water for efficient performance and economy. The use of hard water for dilution and dispersion will often double the required addition of anti-foam and may cause coagulation of the anti-foam and greatly aggravate sticking problems similar to those from pitch. Anti-foams should be used as near ahead of the trouble spot as possible and it is often advantageous to make the addition in smaller amounts at several points in the system rather than all at one location. Spraying of a dilute dispersion (a fine mist) of anti-foam on to the wire 2–3 ft from the slice will produce dramatic effects, if microfoam restricts drainage and causes the dandy roll to throw water and stock. The anti-foam not only reduces surface foam, but increases the rate of drainage through the wire and through the dandy roll. Almost the instant the spray is turned on, the wet line on the wire moves toward the slice and throwing of stock from the dandy roll stops. If the spray is momentarily turned off, the wet line immediately moves further down the wire and the dandy again throws stock. Approximately 0.5 lb anti-foam per ton of stock will effect the change.

A considerable amount of empirical information is available about foam problems in the paper industry,^(131–134) but comparatively little fundamental study has been made of the factors that influence foam stability. This is a worthy field of study.

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Transcription of Discussion

Discussion

Mr J. W. Swanson—Thank you for bringing out these points. I apologise for not having included them in the paper, because they form an important contribution.

There remains the question, however, whether or not sufficiently fractionated resins were used in the study and whether or not the low molecular weight materials that contribute nothing to wet strength and are only partly absorbed were the migrating molecules.

We have done little work on the formation of chemical bonds in the wet strengthening process ourselves, but merely quoted the work of Stannett and co-workers. Their work indicated that very few chemical bonds were formed, though, it will be recalled, quantitative yields of their model products were not obtained. The recovery of, say, the glucoside products was only 95 per cent and the wet strengthening mechanism may not require a large amount of chemical bond formation. I think the work Back has done on high temperature treatment of paperboard indicates quite clearly that chemical bonds are formed and there is little reason to doubt that some chemical bond formation may occur during the development of wet strength.

Dr F. L. Hudson—On the point about fractionation, the resins were ordinary commercial materials and not fractionated. Nevertheless, it was possible to confirm the migration effects indirectly by strength tests, when drying conditions were adjusted to reduce migration.

Miss S. Schmidt—With reference to this paper, the Editor of *Wochenblatt für Papierfabrikation*, Dr. Ulrich Kirchner would like to advise that his doctoral thesis, prepared under the guidance of Prof. W. Brecht, was 'The air content in paper stock suspensions'. They published their results in *Wochbl. Papierfabr.*, 1959, **89** (8), 295–305 and *Das Papier*, 1961, **15** (10a), 625–634.

In November 1964, a round table discussion exclusively concerned with the significance of the air content of paper stock suspensions took place at the Institut für Papierfabrikation of the Technische Hochschule, Darmstadt, organised by the Akademische Papieringenieurverein, of which a detailed report was published in *Wochbl. Papierfabr.*, 1965, **93** (1), 1–22.

Prof. B. G. Rånby—I find it highly commendable to take a positive attitude towards papermaking additives that are being developed by the chemical industry. I agree with Swanson that the paper industry as a whole would benefit by taking advantage of this offer from the chemical industry. In our laboratories, we have studied a few aspects of the large problem of chemical additives, in particular the addition of latices and dry strength resins to papermaking fibre slurries. You cannot expect effects on the paper properties from fine chemicals that are not retained in the papers. Therefore, we have studied retention in detail with many unexpected findings as a result.

When alum is used as a retention aid, it is not only a question of the slurry's pH value, it is also a question how the alumina flocs formed interact with the fibres and the additives (such as the latex particles or the polymer molecules). We have found that there were extremely narrow pH intervals in some cases that gave a retention approaching 100 per cent. In other cases, one could hardly find such an area of high retention, apparently because there is a delicate balance of the pH value affecting the alum in solution *and* the charge of the fibres and the latex particles. The success or failure of using additives may depend upon the retention. These problems can also be so difficult to resolve that they need special studies. Along these lines, you may explain many of the disappointing results with chemical additives.

Mr W. F. Reynolds—Where the use of hydrophilic polymers as fibre defloculants is discussed in Swanson's paper, it may be of some interest to note that it is now possible by the use of a small amount of polymer to control the drainage rate of unbeaten pulp to any degree desired.

Chairman—Time has expired with many questions left unanswered; however, Swanson's slide on the effect of mannogalactans on papermachine formation show clearly that the formation of the machine-made sheet can be influenced chemically.