Preferred citation: V. Balodis, A.W. McKenzie, K.J. Harrington and H.G. Higgins. Effects of hydrophilic colloids and other non-fibrous materials on fibre flocculation and network consolidation. In Consolidation of the Paper Web, *Trans. of the IIIrd Fund. Res. Symp. Cambridge, 1965*, (F. Bolam, ed.), pp 639–686, FRC, Manchester, 2018. DOI: 10.15376/frc.1965.2.639.

EFFECTS OF HYDROPHILIC COLLOIDS AND OTHER NON-FIBROUS MATERIALS ON FIBRE FLOCCULATION AND NETWORK CONSOLIDATION

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Synopsis-Non-fibrous materials used in papermaking are considered under the headings of colloids (positive or negative, hydrophilic or hydrophobic), surfactants (cationic, anionic or non-ionic), electrolytes and other non-polymeric materials. Their effects on flocculation of fibres are discussed in terms of entanglement, bridging and electrokinetic theories of fibre interaction. Various methods of measuring the heterogeneity of pulp suspensions and paper sheets are reviewed and it is concluded that the beta-ray scanning method offers several advantages for paper studies. In this work, the heterogeneity of handsheets made from shortfibred and long-fibred pulps has been determined with a beta-ray scanner (Pm¹⁴⁷ source). The experimental results showed that flocculation was more pronounced in the long-fibred pulps, but that the reduction in paper strength with increasing heterogeneity is greater in the short-fibred paper. Scanning across the handsheet diameter revealed that in some sheets the observed heterogeneity is partly due to systematic variation. In the study of electrokinetic properties of fibre/water interfaces, two parameters-zeta-potential and ionic charge density in the double layer—have been evaluated for alum-treated and polyamide-treated pulps. The results indicate that the variation in zeta-potential with additive concentration is primarily related to charge on the fibre surface for the polyamide-treated pulps and to electrolyte concentration for the alum-treated pulps. The effect of nonfibrous materials on consolidation is considered in terms of surface tension, fibre collapse and hydrogen bonding. Preliminary work on the effect of cationic starch on fibre strength is reported and a method of obtaining lateral load/compression curves of single fibres is described. The curves can be compared to those observed with tubes of differing wall thickness and elastic modulus. Experiments on the effect of modified starches and starch fractions on interfibre bonding are also described; these lead to the conclusion that the bonding efficiency depends on the state of dispersion of the colloid, the internal cohesion of the dried colloid film and the adhesion at the colloid/fibre interface.

Introduction

IN PLANNING this symposium, the organisers have arranged for a division of labour among the contributors to the session devoted to the effects of non-fibrous materials on formation and consolidation. It has been agreed that Swanson⁽¹⁾ shall cover the effects of soluble materials and Schwalbe⁽²⁾ the effects of sizing, adhesive and fillers; our own contribution will review some specific topics, but will be concerned mainly with work carried out recently in this laboratory. The comprehensive nature of Swanson's contribution, which supplements a valuable discourse on the science of additives in papermaking⁽³⁾ published in 1961 and of Schwalbe's paper render unnecessary any attempt at a complete coverage of the subject here.

In the papermaking field, non-fibrous materials are normally classified according to the purpose for which they are used and are taken to include sizes, beater additives, fillers, pigments, dyestuffs, etc. Their purpose is not usually related to the processes of formation or consolidation, however, except in special cases such as that of the galactomannan gums; it is therefore appropriate to the present discussion that they should be classified according to their physico-chemical properties rather than to their various purposes. Furthermore, if we proceed from the assumption that the dominant factors in formation and consolidation (under similar hydrodynamic conditions and at the same concentration and temperature) are the mechanical properties of the fibre and the state of the fibre surface, then it is logical to consider nonfibrous materials in groups whose members would be expected to have similar effects on these fibre characteristics.

The grouping to which we shall adhere, then, is the following-

Colloids(positively or negatively charged, hydrophilic or hydrophobic)Surfactants(cationic, anionic and non-ionic)ElectrolytesOther non-polymeric compounds

After a brief discussion of the role of these materials in papermaking, the processes of flocculation and consolidation will be considered, together with the results of experiments on the measurement of heterogeneity, zeta-potential, the role of surface tension, the mechanical properties of fibres in lateral compression, changes in dimensions on consolidation and paper properties. If possible, new data on the effect of non-fibrous materials will be introduced.

Non-fibrous materials in papermaking Colloids

Most wet end additives are present in colloidal form during the processes of formation and consolidation. Four basic types may be distinguished, as

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indicated above. Typical of the negative-hydrophilic colloids are the carbohydrate additives, resin size and some wet strength resins; examples of the positive-hydrophilic group are cationic starches, cationic wet strength resins and polyamide retention aids. The negative-hydrophobic group includes most inorganic fillers and pigments and additives such as the synthetic and natural rubber latices. Few positive-hydrophobic colloids are found; even colloidal alumina can more properly be classified as hydrophilic.

The effect of colloidal materials on the mechanical properties of the fibre is limited by their inability to penetrate into the interior of the fibre to any marked extent; thus, they will contribute to these properties in only an additive way—except perhaps where they may reinforce weak points in the fibres, but this is unlikely to occur to any large extent in the wet state.

The principal effect of colloidal materials, with respect to formation and consolidation, is to alter the state of the fibre surface. It is well known that a colloidal substance when adsorbed on to a surface will impart to the surface the electrokinetic properties of the colloid itself.⁽⁴⁾ The interfibre adhesion properties of the wet fibre may also be modified in the direction of those of the adsorbed colloid, but such effects are complex. Hydrophobic colloids may be expected to decrease adhesion, but the effect of hydrophilic colloids may depend on factors such as their adhesive capacity compared with cellulose and its associated polysaccharides and their ability to form bridges according to the postulates of La Mer and his co-workers.⁽⁵⁾ The charge on the colloid might be expected primarily to affect its retention, positively charged colloids being, in general, more effectively adsorbed than negative colloids on to a negative surface. A distinction should be made between attraction and adsorption, however, because—as Swanson points out⁽¹⁾—the colloid can be drawn to the fibre without being strongly adsorbed. Negative colloids may require the presence of a retention aid, which is usually also colloidal in nature: in this case, the properties of the mixed system are those that influence the final state of the surface. From the viewpoint of those workers who regard zeta-potential as a controlling factor in flocculation, the magnitude of the charge on the fibre, rather than the sign, is the important consideration: adsorbed colloids of opposite charge to the fibre can, with increasing retention, first reduce the zeta-potential to zero, then increase it in the opposite sense, so that any effect on flocculation would eventually be eliminated.⁽⁶⁾ It is important to stress in this context, however, that flocculation and network formation can take place without the intervention of electrical forces as shown by the studies of Wahren and his associates in Steenberg's laboratory.⁽⁷⁾

Surfactants

Surfactants are used in a papermaking furnish primarily as wetting agents

to overcome the hydrophobic properties imparted to the system by other additives such as wet strength resins. In some instances, they may behave rather like colloids, being adsorbed on the fibre and modifying its surface characteristics, adsorption increasing in the direction anionic—non-ionic— cationic.⁽⁸⁾ Reduction of surface tension would be expected to affect the formation process, for example, by decreasing the compacting forces as the air/water interface is drawn down through the fibre pad.⁽⁹⁾

Electrolytes

Electrolytes are present in all papermaking systems. Some, such as alum and calcium salts, are added for a specific purpose; others are introduced in the water supply as components of other additives or in the pulp itself. The effect of electrolytes on fibre properties may be predicted in general terms, if the fibre is considered to behave as a negatively charged gel particle.⁽¹⁰⁾ Cations will affect the surface potential, also the swelling equilibrium within the fibre to an extent depending on their concentration and valency. Anions will have little direct effect, but they will affect the behaviour of any positively charged colloids introduced into the system. Similarly, cations will modify the behaviour of any negative colloids introduced. In addition, polyvalent cations may, under appropriate conditions, be converted to colloids (say, alum to alumina) and their behaviour under these conditions will be no longer that of an electrolyte, although some free electrolyte will in most cases also be present.

Other non-polymeric compounds

Certain compounds of low molecular weight, other than electrolytes, also have an effect on the fibre surface on to which they may be adsorbed. The smallness of the molecule may allow them to penetrate into the body of the fibre and thereby alter its mechanical properties.⁽¹¹⁾ In this category are dyes, optical brighteners, plasticisers, softening agents and similar materials.

Flocculation

Sedimentation conditions

Erspamer,⁽¹²⁾ in early experiments on flocculation, showed that the heterogeneity of handsheets is linearly related to the time interval between the final stirring of the pulp suspension and the completion of drainage. It has also been shown⁽¹³⁾ that the degree of flocculation of a pulp suspension is directly related to the heterogeneity of handsheets made from the suspension. The most extensive work on flocculation under sedimentation conditions has been carried out by Andersson.⁽¹⁴⁾ Essentially, this work is based on concepts of fibre collisions and flocculation emerges as a consequence of such collisions, which result from different sedimentation velocities of individual fibres and fibre aggregates. An equation was theoretically derived for the increase in flocculation with sedimentation time; the qualitative aspects of this equation have been confirmed experimentally. Fibre length, viscosity and density difference between fibres and liquid were shown to influence flocculation rate in the manner predicted. It may be noted, however, that Andersson's model provides only the mechanism of collisions and is not concerned with the cohesion of fibres after collision.

Flow conditions

When a pulp suspension at papermaking consistency is pumped along a pipe, flocculation is observed at some distance from the inlet.⁽¹⁵⁻¹⁸⁾ A similar effect is observed when the pulp suspension is placed between rotating cylinders.⁽¹⁸⁻²⁰⁾

Mason and co-workers^(17, 18, 20) have carried out extensive theoretical work under flow conditions with the primary aim of determining the factors that control the collision frequency of fibres. An equation has been derived showing that collision frequency depends on the shear gradient, the fibre volume, a geometrical shape factor and the square of the number of particles per unit volume. Experimental results show⁽¹⁶⁾ that flocculation increases with fibre length (which affects the shape factor and the fibre volume), with concentration and with the shear gradient, so that Mason's equation is in qualitative agreement with observations.

Nature of networks and flocs

Wahren,⁽⁷⁾ on the basis of extensive investigations of three-dimensional networks, in association with Thalén, Meyer and Raij, has advanced the view that fibre networks are coherent mainly through physical bonding caused by entanglement of the fibres. More specifically, the fibres adhere because of internal stress, which arises when a fraction of the fibres comes to rest during the flocculation process in strained positions, so that forces can be transmitted from fibre to fibre.

Less specific entanglement theories have been previously proposed, but the interesting feature of Wahren's approach is that a source of the energy of network cohesion is provided by the strained fibres, which have become deformed during the agitation that precedes flocculation. Without attempting to evaluate the detailed aspects of this hypothesis—one consequence of which is that a clear distinction can be drawn between the internally stressed network or floc and an incoherent heap of fibres such as might be deposited from very dilute suspension—we can certainly recognise the importance of fibre entanglement in flocculation and the experimental fact that flocculation can take place in situations in which only mechanical interaction is possible.

Concerning the effect of non-fibrous materials on flocculation, an important question is whether mechanisms other than the mechanical interactions can also contribute to this phenomenon. Interfibre adhesion has been ascribed to the properties of fibre surfaces and to fibre-colloid interactions; the various theories were summarised by Robertson & Mason⁽²¹⁾ at the Oxford symposium and they have been discussed by Balodis.⁽²²⁾

Information is sparse on the effect on flocculation of the physical state of the fibre—for example, fibrillation and degree of swelling—but such factors would be expected to have some influence. It is difficult to assess their significance independently, as most treatments such as beating change several relevant properties simultaneously.⁽²³⁾

The electrical properties of the fibre deserve careful attention in any assessment of the role of additives in formation. In distilled water, cellulose fibres behave as negatively charged particles⁽²⁴⁾ and therefore (a) the fibres will tend to repel each other and, before contact can be established, this repulsion will have to be overcome by mechanical or other forces and (b) ionic material and charged colloids will be attracted or repelled by the fibres, depending on the sign of the charge. The adsorption of such material will change the surface potential of the fibres and may thus change their flocculation behaviour.

It has been shown that under some idealised conditions the electrokinetic or zeta-potential (Z.P.) may control the flocculation of pulp suspensions. For example, $Erspamer^{(12)}$ observed that in benzene (Z.P.=0) the pulp formed large flocs that could not be dispersed into fibres even with very vigorous stirring, whereas on replacing the benzene with nitrobenzene (Z.P. = 142 mV)the fibres dispersed and remained dispersed for a considerable time. Under conditions similar to those employed in practical papermaking, the role of zeta-potential in flocculation is very difficult to assess. The difficulties may be illustrated by considering the effect of alum on fibre flocculation, which, under various conditions, has been shown to depend on temperature,⁽¹²⁾ pH value of the suspension,⁽²⁵⁾ concentration,⁽¹²⁾ impurities in the water⁽¹⁵⁾ and time of standing.⁽¹⁵⁾ The presence of alum increases flocculation at 8°C and decreases it at 60°C. Alum acts as a dispersing agent in the pH range 4.5-9.0 and as a flocculating agent outside this range.⁽²⁵⁾ At low concentrations, it acts as a dispersing agent, but as a flocculant at higher concentrations.⁽¹²⁾ Flocculation is greater in distilled water than in tap water.⁽¹⁵⁾ After dispersion with alum, the suspension was found to flocculate again when allowed to stand.⁽¹⁵⁾

Although it is possible to interpret some of these observations in terms of zeta-potential by taking into account the fact that alum is amphoteric and capable of forming both cations and anions of different valency⁽²⁶⁾ and by noting that alum reacts with the calcium and magnesium ions in tap water.⁽⁶⁾

the general impression is that the simple zeta-potential model does not fully explain the behaviour of alum/fibre systems.

The role of zeta-potential in flocculation becomes very questionable in fibre/starch systems. Starch, although a negative colloid, increases flocculation.⁽¹²⁾ To explain this observation, the zeta-potential model may have to be replaced by a model such as the one discussed by La Mer & Healy.⁽⁵⁾ According to this concept, a segment of the polymer is adsorbed on to the fibre surface and another segment of the same molecule is adsorbed on to an adjacent fibre, thus forming a bridge. In this model, the zeta-potential of the fibres and of the polymer probably influence the rate of adsorption, but the equilibrium is controlled by interactions of a more chemical nature. La Mer & Healy state that 'the chemical interactions which operate in flocculation are very intense at short range and are of sufficient magnitude to overwhelm the electrostatic repulsion between particles having net charges of the same sign'.

This chemical interaction model may not be restricted to the explanation of the role of polymers, because experiments have shown that colloids such as bentonite and aluminium hydroxide probably interact with fibres in a similar manner. For example, it has been observed that flocculation increases with the addition of bentonite⁽¹⁵⁾ and that it passes through a maximum with increasing alum concentration⁽¹²⁾ and with prolonged mechanical agitation at a fixed alum concentration. The observations on the effect of alum on fibre flocculation are of particular interest. According to La Mer & Healy,⁽¹⁵⁾ bridging increases to a maximum with increasing polymer concentration, then declines as the fibres become completely coated. At a constant polymer concentration, bridging first increases with mechanical agitation, then decreases with further agitation. These changes in the degree of bridging would be manifested as an initial increase in flocculation, followed by a decrease, which is similar to the observed behaviour of some fibre/alum systems. It is also conceivable that detached fibre fragments behave as colloidal material and would be capable of forming bridges between fibres; hence, it may be possible to extend this model to the study of fibre suspensions free of additives.

The bridging concept appears to provide a more satisfactory explanation of the behaviour of systems whose components have the same charge than any theory based solely on electrokinetic properties. Electrical surface potentials may well tend to keep fibres apart, but it is difficult to conceive a mechanism that will account both for the fibres being attracted towards each other and for the necessary interfibre adhesion. In such systems, it may well be that the role of zeta-potential is only to oppose flocculation and that the mechanism of network cohesion will have to be sought in other physical and chemical properties of the fibre surface or in internal stresses as advocated by the Swedish school.⁽⁷⁾

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The ability of fibres to adsorb colloids of the same electrical sign is demonstrated by the adsorption of starch by cellulose,⁽²⁷⁾ also by the charge reversal occurring during the adsorption of polyamides⁽⁶⁾ and chrome glue.⁽²⁸⁾ The data given by Carolane⁽²⁸⁾ on the effect of alum and chrome glue on freeness provide evidence for the bridging mechanism when plotted in the form shown in Fig. 1. If the Canadian standard freeness is taken as a measure of the degree



Fig. 1—Effect of zeta-potential on freeness for pulps in the presence of chrome glue and alum

of flocculation (see below), it can be seen that for alum, which would not be expected to give rise to bridging to the same extent as the polymeric chrome glue, the flocculation tends towards a maximum value in the vicinity of zero zeta-potential. The maximum for the chrome glue is well removed from zero zeta-potential, however, presumably occurring at a point corresponding to the surface cover of the fibre that is optimum for bridging.

Measurement of heterogeneity

Various indirect methods are available⁽²²⁾ for assessing the degree of flocculation from some other property of the pulp suspension; these usually have the advantage of requiring only simple equipment. The sedimentation volume of a flocculated suspension of colloidal material is greater than that of a non-flocculated suspension⁽²⁹⁾ and this observation may have application to pulps. Filtration rate also increases with the degree of flocculation of colloids.⁽⁵⁾ The filtration rate of a pulp suspension as measured by free 1 c

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tends to a maximum value as the zeta-potential of the fibres approaches zero⁽³⁰⁾ and flocculation is also at a maximum at this point.⁽¹²⁾ These observations suggest that a rapid assessment of flocculation in pulp suspensions under comparable conditions might be obtained by such means, but filtration behaviour is so susceptible to the presence of fines and colloids that it would be difficult to specify comparable conditions.

Wollwage⁽¹⁵⁾ used another relatively simple method in one of the first fullscale experiments under flow conditions. The pulp suspension was pumped down a vertical pipe in a closed circuit and the distance from the inlet to the point at which obvious flocculation occurred was measured at a number of velocities; from these data, a dispersion index could be calculated. This method has the advantages of simplicity and applicability to a considerable range of concentrations, but the physical meaning of the dispersion index is rather obscure. Subsequent experiments⁽¹⁶⁾ on the flow of dilute suspensions showed that the distance at which the rate of floc formation is equal to the rate of floc dispersion depended on the flow velocity. The distance/velocity curve passes through a maximum corresponding to the mixed flow regime. These later findings tend to complicate the simple interpretation assigned to the index by Wollwage, but, within a given flow regime, the method may still have useful applications.

The heterogeneity of paper can also be measured indirectly in various ways —for example, by the use of a smoothness tester, by filling the surface irregularities with a material such as ink and measuring the reflectance characteristics⁽³¹⁾ or by incorporating iron oxide in the coating material and measuring the magnetic permeability.⁽³²⁾ Such tests have been used primarily for quality control.

Among the direct methods of studying flocculation of suspensions and heterogeneity of paper, the most widely used has been the optical transmission method,^(14, 17, 20, 33-38) in which the transmitted light is detected by a photocell and the cell output recorded as a trace or the ac and dc components of the photocell current are separated and read directly. In either case, a flocculation index ν can be calculated from the readings. This index utilises only a fraction of the information contained in the trace, the analysis of which can be extended to give floc size and concentration,⁽³⁸⁾ a frequency diagram of floc size, a test for non-random components, etc. If the trace has a systematic component and the object is to assess random fluctuations, then it may be necessary to establish the frequency of the non-random component by means of an auto-correlation function⁽³⁸⁾ and to remove this component from the complete trace by the application of Fourier analysis. If the object is to study systematic components, a frequency diagram⁽³³⁾ may provide the most useful record of paper heterogeneity. For handsheets, it might be thought that the systematic component should be negligible; unfortunately, as shown below, this is not always so.

From the theory of random pulses, the Canadian workers,^(17,20) have derived two parameters for the classification of random aggregates: the coefficient of variation ν (flocculation index) and the average distance between neighbouring crossings of the signal trace and the mean signal (1/N), which is related to floc size. Since the use of dual indices complicates the direct comparison of different pulps, an attempt has also been made⁽¹⁷⁾ to combine ν and N, to define flocculation index as (ν/N). As shown elsewhere,⁽²²⁾ this procedure may fail to distinguish between traces showing different patterns; a similar objection holds if the parameters are combined in the form (νN). Hence, it may be necessary to retain the dual index, except when one of the parameters remains relatively constant.

Although extremely useful, the optical scanning method has several disadvantages. The study of flocculation under flow conditions is restricted to low pulp concentrations, so that the total absorption does not overshadow the variation in transmitted light. When the method is applied to paper, the samples should be of the same colour and transparency, otherwise the direct comparison of different batches of paper becomes very difficult. Furthermore, the intensity of transmitted light depends on the density of the paper as well as on the mass per unit area; a good example of this effect is given by Tydeman & Hiron.⁽³⁹⁾

Beta-ray scanner

There appears to be no easy solution to the problem of measuring flocculation under flow conditions, but for paper the use of a beta-ray gauge has certain advantages over the optical method. The first of these is that it will provide a measure of mass per unit area, so that the index may be expressed in absolute rather than in relative units. Furthermore, provided normal care is taken, the results from the beta-ray scanner can be compared directly for different types of paper and for different laboratories, without the need for standardisation of the equipment by a central agency.

The beta-ray scanner has been used successfully on thin wood samples; the most frequently used beta-ray sources have been strontium- $90^{(40-42)}$ and carbon-14.⁽⁴³⁾ Of these two sources, C-14 appears to be more suitable for ordinary handsheets, because of its lower energy beta-radiation (0.155 MeV against 0.61 MeV for Sr-90). Nickel-63 (0.067 MeV) and promethium-147 (0.22 MeV) would also provide suitable sources.

To test the feasibility of using a beta-ray scanner for flocculation measurements, experiments have been carried out, in collaboration with the Australian Atomic Energy Commission, with a Pm-147 beta-ray source. The instrument used for these experiments is shown diagrammatically in Fig. 2. The paper samples are moved by a scanning device, constructed according to the design of Phillips *et al.*⁽⁴¹⁾ The paper can be scanned in a straight line at rates of 1, $\frac{1}{2}$, $\frac{1}{4}$ or $\frac{1}{8}$ cm/min by means of a screw attached to a synchronous motor. The source apertures available are 2, 1 and $\frac{1}{2}$ mm in diameter. The total scan length is 25 cm. The source was calibrated with airmail paper over the range 18–110 g/m². The calibration curve is shown in Fig. 3.



Fig. 2-Diagram of the source and detector arrangement of the beta-ray scanner



Fig. 3—Calibration curve for the beta-ray scanner

Flocculation experiments

Materials—The flocculation studies were carried out on test strips prepared from standard British handsheets (nominal substance 60 g/m²). The handsheets were formed in distilled water from *Pinus radiata* and *Eucalyptus regnans* kraft pulps beaten for 200 rev in the PFI (about 530 rev/min housing

speed, 1.8 kg/cm load) and 1 125 rev in the Lampén mill, respectively. The appropriate additives were introduced after beating and the pulp suspension was agitated in a stock divider for 15 min before forming the sheet. The papers used in the flocculation measurements are listed in Table 1.

Identification	Type of paper	Settling time, sec	Additives, ppm in machine stock
PR-10 PR-35 PR-60 PR-85 PR-110 E-10 E-35 E-60 E-85 E-110 A-0 A-10 A-25 A-50 A-100 A-500 P-0 P-1 P-1 P-5 P-10 P-1000 P-1000	P. radiata kraft " " " " " " " " " " " " " " " " " " "	$ \begin{array}{c} 10\\35\\60\\85\\110\\10\\35\\60\\85\\110\\35\\35\\35\\35\\35\\35\\35\\35\\35\\35\\35\\35\\35\\$	0 0 0 0 0 0 0 0 0 0 0 0 0 0

TABLE 1-LIST OF PAPERS USED IN FLOCCULATION EXPERIMENTS

* Al₂(SO₄)₃.18H₂O

Test procedure and results—For the series PR-10 to E-110, two handsheets were prepared; for the additive series A-0 to P-1000, the tests were carried out on a single handsheet. Two test strips were cut from each sheet for flocculation measurements and subsequently used for the determination in the D.F.P. rheometer of an elastic modulus E and tensile strength T. (In this paper, E and T are not Young's modulus and tenacity, but are expressed in terms of solid fraction⁽⁴⁴⁾ by assuming that the density of this solid fraction is 1.5 g/cm³ and that the substance \overline{M} for a given test strip is the value obtained from the beta-ray scanner.) The remaining portions of the sheets were used for air resistance measurements (Gurley-Hill SPS tester).

The flocculation measurements were carried out at a scanning rate of about 1 cm/min and with a source aperture of about 2 mm. Before each day's scanning, a calibration test strip (in the form of a stepped wedge prepared from high quality paper at about 18 g/m² in substance) was run through the apparatus. The observed count rate n (per sec) for the calibration strip and

the test strips was converted to true count rate n_0 by allowing for the preset paralysis time ($t=2 \times 10^{-4}$ sec) by means of the equation—

$$n_0 = n/(1-nt)$$
 . . . (1)

The mass per unit area M was then calculated from the equation-

$$M = a \log n_0 + b \qquad . \qquad . \qquad . \qquad (2)$$

where a and b are calibration constants.

The variation with scanning distance in mass per unit area for typical test strips is shown in Fig. 4 for the E series, Fig. 5 for the PR series and Fig. 6



Fig. 4—Mass profiles for E. regnans handsheets made after varying settling times

for the P series. The flocculation index for the test strips was calculated from the equation—

$$\nu = \frac{\{(\overline{M} - \overline{M})^2\}^{\frac{1}{2}}}{\overline{M}} \times 100 = \frac{\sigma_M}{\overline{M}}(3) \times 100 \qquad . \qquad . \qquad (3)$$

where the M values were read from the traces of M against scanning distance at approximately 0.1 cm intervals. The same values of M were used to determine floc size (1/N) from the equation—

$$N = \frac{1}{\sigma_M \pi (dS)} \{ (\overline{dM})^2 \}^{\frac{1}{2}} \qquad . \qquad . \qquad (4)$$

where dM denotes the change in mass per unit area at two successive locations distance dS apart (see Table 2).

Symbols	S	\overline{M}	ν	1/N	E	Т	A.R.
Identifi- cation	Total scan, cm	Subst- ance, g/m ²	Flocculation index, per cent	Floc size, cm	Elastic modulus 10 ¹⁰ dyn/cm ²	Tensile strength, 10 ⁸ dyn/cm ²	Air resist- ance, sec
PR-10 35 60 85 110	60 60 60 60 60	59.9 58.8 61.2 60.5 57.2	3.0 4.6 6.0 7.2 9.5	0.59 0.83 0.83 0.83 1.1	6.60 6.77 6.50 6.58 6.10	7.84 7.46 6.56 7.32 6.98	3.2 3.5 3.8 3.9 4.8
E-10 35 60 85 110	60 60 60 60 60	60.3 58.7 62.7 62.1 60.7	1.7 1.8 2.0 2.6 3.3	0.56 0.62 0.59 0.67 0.67	7.79 8.37 7.80 7.05 6.83	7.28 6.62 6.35 5.57 6.00	3.1 3.4 3.4 3.3 3.1
A-0 10 25 50 100 500	30 30 30 30 30 30 30	62.0 61.4 57.2 58.6 61.4 59.2	4.8 5.2 5.0 6.2 4.4 4.9	1.0 0.91 0.91 1.0 0.71 0.83	6.90 6.64 6.84 6.70 6.82 7.24	6.64 6.68 7.34 6.98 7.36 7.62	3.7 2.9 2.6 3.3 3.3 4.0
<i>P</i> -0 1 5 10 100 1000	30 30 30 30 30 30 30	60.4 61.8 60.1 63.6 63.6 63.6 63.6	3.6 4.8 4.2 7.4 4.8 5.0	0.62 0.83 0.71 1.5 1.0 1.0	6.84 6.78 6.96 6.24 7.37 6.60	7.58 7.94 7.46 6.60 8.08 8.80 8.80	4.0 3.4 3.2 3.8 4.1 3.7

TABLE 2-RESULTS	OF FLOCCU	LATION AND	STRENGTH	TESTS



Fig. 5-Mass profiles for P. radiata handsheets made after various settling times



Fig. 6—Mass profiles for P. radiata handsheets made in the presence of different concentrations of polyamine

Change in flocculation index with settling time and additive concentration— The present results (Fig. 7) confirm those of other investigators, $^{(13, 36, 38)}$ in that the degree of heterogeneity in handsheets increases linearly with increasing settling time. Statistically, the linear relationship accounts for 84 per cent of the variation in ν with settling time for the PR series, and 60 per cent for the E series. Extrapolating to zero settling time for the PR series, $\nu=2.3$ per cent; for the E series, $\nu=1.3$ per cent. In addition, the rate of increase in heterogeneity for the PR series is approximately four times as great as that for the E series.



Fig. 7—The influence of settling time on the heterogeneity of *E. regnans* and *P. radiata* handsheets



Fig. 8—The influence of settling time on floc size (1/N) in *E. regnans* and *P. radiata* handsheets



Fig. 9—The influence of settling time on the tensile strength of *E. regnans* and *P. radiata* handsheets

For the E series, floc size remains relatively constant and statistically the trend shown in Fig. 8 is not significant, whereas for the PR series there is a significant increase in floc size with settling time.

From the above results, we can conclude that under laboratory conditions the heterogeneity of paper made from long-fibred pulp is greater than that of paper made from short-fibred pulps. In fact, the paper made from *E. regnans* at 110 sec settling time has approximately the same degree of heterogeneity as paper made from *P. radiata* pulp under standard conditions (10 sec settling



Fig. 10—The influence of settling time on the elastic modulus of *E. regnans* and *P. radiata* handsheets

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time)—Table 2. Furthermore, the aggregate size increases appreciably with settling time for the *P. radiata* pulp.

The results in Table 2 show no significant effect of additive level on the degree of heterogeneity of paper made from these treated pulps.

Effect of settling time and degree of heterogeneity on strength properties and air resistance—It has been shown^(13,38) that in general the strength of paper decreases with increasing settling time and the present results confirm these observations. As can be seen in Fig. 9 and 10, both elastic modulus E and tensile strength T decrease with settling time.

It is of interest to note that the change in strength with settling time (Fig. 9 and 10) is different for the two pulps, the most rapid decrease in strength properties being exhibited by the *E. regnans* pulp. This is somewhat surprising, in view of the heterogeneity against settling time results, among which the most marked change occurs for the *P. radiata* pulp. From these observations, we may conclude that the strength properties of paper are strongly dependent on an interaction between fibre length and heterogeneity.

To assess the effect of heterogeneity on strength properties, linear equations were calculated relating ν to E and T for the following two types of pulp—

P. radiata

 $T = (-0.110\nu + 7.90) \times 10^{8} \text{ dyn/cm}^{2} \qquad (r = -0.33)$ $E = (-0.084\nu + 7.02) \times 10^{10} \text{ dyn/cm}^{2} \qquad (r = -0.45^{*})$ *E. regnans* $T = (-0.492\nu + 7.48) \times 10^{8} \text{ dyn/cm}^{2} \qquad (r = -0.51^{*})$ $E = (-0.499\nu + 8.71) \times 10^{10} \text{ dyn/cm}^{2} \qquad (r = -0.56^{**})$

where r is correlation coefficient and * and ** denote significance at P=0.05 and P=0.01 probability levels, respectively.

These results confirm the observation that the effect of heterogeneity on strength properties is markedly different for the two pulps. Yet, because of the large scatter in the experimental results (as indicated by the low correlation coefficients), a more extensive sampling may have to be carried out in subsequent experiments in order to establish these relationships to a higher degree of reliability.

A possible reason for the reduction in strength as a result of heterogeneity would be the greater likelihood of finding low strength zones in a highly heterogeneous paper. This possibility was tested by trying to relate the strength of a given test strip to the lowest substance value as determined on the beta-ray scanner. No significant correlation could be established between T or E and M_{\min} .

The effect of additive on strength properties shows no significant trends (Table 2).

Air resistance increases with settling time for the PR series, but follows no significant trend for any of the other series (Table 2).

Effect on flocculation index of systematic variation in test strips—In a number of cases, such as Fig. 6 trace P-1, Fig. 5 trace PR-110, the traces exhibit central symmetry, which may imply that the heterogeneity as measured on handsheets is not wholly due to random flocculation, but may be partly due to systematic variation as a result of the action of the sheetmachine. For



Fig. 11—Separation of the systematic and random components of the flocculation index for a handsheet scanned across a diameter (sheet PR-110)

example, the grid under the sheetmachine wire may produce systematic patterns, which would in some cases overshadow the random variation. On the assumption that central symmetry results from systematic factors in the sheetmachine, the trace corresponding to PR-110 (Fig. 6) has been analysed

geometrically in Fig. 11. The original trace is shown in trace A and a calculated linear component in trace B. When this linear component is removed from trace A and the two halves of the trace are superimposed (trace C), the shaded areas are common to both sides. If these common areas are due to systematic variation, then the original trace (after removal of the linear component) can be split up into a systematic component (trace D) and a random component (trace E). The value of ν for the trace E is 4.9 per cent, whereas, for the original trace (A), $\nu = 10.2$ per cent. Hence, the systematic component contributes considerably to the total variation and it appears therefore that the study of flocculation by means of handsheets may not always be very reliable.

Electrokinetic properties of fibre/water interfaces Apparatus

To investigate the electrokinetic properties of fibre surfaces, an instrument similar to that used by Hästbacka & Nordman⁽³⁰⁾ has been assembled. The instrument consists of a 1 in precision bore borosilicate glass tube in which are fitted two accurately machined, perforated and anodised (HCl) silver electrodes. The concentration of the pad is changed by altering the distance between the electrodes. The pressure drop across the pad is controlled by a



Fig. 12-Diagram of apparatus for measuring zeta-potential

needle valve and the flow of electrolyte through the pad is measured on a tri-flat flow meter (Fig. 12).

The current generated by the flow is measured as a voltage drop across a resistance parallel to the pad on a Philips GM 6020 millivoltmeter. To ensure satisfactory operation, all the electrical leads are shielded.

Experimental procedure

(a) The pressure drop across the electrodes without a pad was determined over a range of flow rates and the measured pressure drops across the pad were adjusted for this pressure loss by the equation—

$$\Delta p = \Delta p_m - aQ \qquad . \qquad . \qquad . \qquad (5)$$

where Δp_m is the measured pressure drop, Δp is the pressure drop across the pad, Q is flow rate and a is a constant of proportionality as determined for the electrode system without the pad.

(b) The pulp was de-aerated before forming the pad to avoid subsequent bubble formation and the electrolyte was filtered to ensure satisfactory operation of the flow meter and needle valve.⁽³⁰⁾

(c) Trial runs showed that the voltmeter zero does not remain constant. Since the flow in the apparatus could not be reversed, the method used by Lewis⁽⁴⁶⁾ to adjust for polarisation voltage could not be used. The method adopted was to measure the voltage drop across a given parallel resistor for a particular pad and pad concentration for a number of Δp values and to relate measured voltage V_m to Δp by—

$$V_m = a\Delta p + \delta V \qquad . \qquad . \qquad . \qquad (6)$$

where a is a regression constant and δV is zero error. Thus, the corrected voltage across a given resistor R_i is—

$$V_i = V_m - \delta V \qquad . \qquad . \qquad . \qquad . \qquad (7a)$$

$$V_i/\Delta p = a_i$$
 (7b)

or

In most of this work, the corrected voltage was calculated from equation (7b).

(d) The pad resistance R_p was determined by measuring the voltage drop across a number of resistors in parallel with the pad⁽⁴⁵⁾ and calculated from—

where R_M = resistance of meter, V_i = voltage across resistor R_i and V = voltage across open circuit. Experimental observations showed that R_p is a linear

function of pad length L and therefore an equation for each pad was evaluated of the form—

$$R_p = BL + D \qquad . \qquad . \qquad . \qquad (9)$$

(e) The streaming current I for a given pad was calculated from—

$$I = V\left(\frac{1}{BL+D} + \frac{1}{R_M}\right) \qquad . \qquad . \qquad (10)$$

Material

The pulp used in these experiments was a moderately beaten *P. radiata* kraft pulp treated with additives according to the A and P series listed in Table 1. One sheet weight (about 1.2 g oven-dry) of pulp was used to form the pad in each case. To ensure satisfactory operation of the silver/silver chloride electrodes, $10^{-3}N$ sodium chloride solution was used in place of distilled water. A control pad was evaluated at the beginning and at the end of each series. To assess the effect of sodium chloride on the electrokinetic properties of fibres, an additional run was carried out with $10^{-4}N$ sodium chloride solution.

Zeta-potential calculations and results

Zeta-potential (Z.P.) was calculated by means of the semi-empirical equation proposed by Biefer & $Mason^{(46)}$ —

$$\left(\frac{I\eta L}{\Delta p D} \cdot \frac{4\pi}{A}\right)^{2/5} = (b\zeta)^{2/5} (1 - \alpha C) \qquad . \qquad . \qquad (11)$$

where the additional symbols are-

 η and D = viscosity and dielectric constant of electrolyte

- A =cross-sectional area of pad
- $b = \text{pad constant } (b \leq 1)$
- $\zeta = zeta$ -potential
- α = specific swollen volume of fibres
- C = pad concentration.

The calculation of Z.P. was carried out in two steps. Firstly, the specific swollen volume was determined for all pads from—

$$V' = K_1 C + K_2 = K_2 (1 - \alpha C)$$
 . (11a)

where V' is the left side of equation (11) and K_1 , K_2 are regression constants. The calculated values of α showed no systematic variation with pad treatment: therefore, for the second step, $\bar{\alpha} = 2.56 \text{ cm}^3/\text{g}$ (coefficient of variation 6.5 per

3--с.р.w. п

cent) was taken as the best estimate of α . With this value of α , the porosity of the pad ϵ becomes (1-2.56C) and equation (11) can be rewritten as—

$$\frac{I\eta L}{\Delta p D} \cdot \frac{4\pi}{A} = b\zeta \epsilon^{5/2} \qquad . \qquad . \qquad (11b)$$

Next, the values of Z.P. were calculated from the intercept of the vertical axis at $\epsilon = 1$. The calculated values of Z.P. are set out in Table 3 and the experimental points are shown in Fig. 13. The reproducibility of the calcu-

Identification	Additive	Additive concentration, ppm	Sodium chloride concentration normality	(bζ), mV
Controls (A-0, P-0) A-10 A-25 A-50 A-100 A-500 P-1 P-5 P-10 P-100 P-1000 N	Alum "" "" Polyamine "" ""	10 25 50 100 500 1 5 10 100 1000 	$10^{-3} \\ 10^{-3} \\ 10^{-3} \\ 10^{-3} \\ 10^{-3} \\ 10^{-3} \\ 10^{-3} \\ 10^{-3} \\ 10^{-3} \\ 10^{-3} \\ 10^{-3} \\ 10^{-3} \\ 10^{-3} \\ 10^{-3} \\ 10^{-4} $	$\begin{array}{r} -7.6 \\ -5.8 \\ -4.0 \\ -2.2 \\ -1.8 \\ -1.3 \\ +2.4 \\ +5.8 \\ +9.5 \\ +14.5 \\ +11.9 \\ -11.0 \end{array}$

TADLE 2 7ETA DOTENTIAL	FOP	MODERATELY	BEATEN F	Pradiata DI II D
IABLE 3-ZEIA-PUIENIIAL	FUR	MODERATELI	DEALEN	, radiala PULP

lated values of Z.P. for the control pads is good (coefficient of variation 4.3 per cent); the accuracy of the other estimates cannot be satisfactorily assessed without further replication.

The results in Table 3 indicate that the effect of alum on Z.P. is similar to that expected from an electrolyte. Qualitatively, a similar effect would be produced by increasing sodium chloride concentration, because according to Neale⁽⁴⁷⁾ the Debye-Hückel approximation—

Z.P.
$$\propto q/n^{\frac{1}{2}}$$
 (12)

(where q = charge on fibre and n = concentration of 1-1 electrolyte) holds for electrolyte concentration of 10^{-3} N and above. From equation (12), Z.P. can be reduced by decreasing charge q or by increasing ion concentration and, although either of these changes may occur in the presence of alum, the increased ion concentration may be sufficient to reduce the Z.P. in keeping with the experimental observations.

The introduction of polyamine must change the charge on the fibre in order to produce a reversal in the polarity of Z.P. As Z.P. increases with increasing

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Fig. 13—Graphs of stream current function plotted against porosity for pulp pads treated with different concentrations of sodium chloride and of alum and polyamine in the presence of $10^{-3}N$ sodium chloride

polyamine concentration (up to P-100), it is possible that this is due to increased charge on the fibre. The observations for P-1000 do not fit this general pattern and the possible reasons for this discrepancy will be discussed later.

Effect of Z.P. on flocculation

Let us return briefly to the flocculation results in the previous section. In view of the Z.P. results, one would expect that, if flocculation were strongly controlled by Z.P., then the maximum flocculation would occur for the A-500 and P-1 samples, followed by a reduction in flocculation with decreasing alum concentration and increasing polyamine concentration. The flocculation results (Table 2) do not follow these expectations.

It cannot be concluded definitely from the above observations that Z.P. does not affect flocculation, because the handsheets were formed at the normal sheetmachine concentration, which in itself tends to keep the fibres from colliding with each other; furthermore, the systematic irregularities in the handsheets may have masked any changes in random flocculation because of Z.P. changes.

A possible effect of the additives may be the slight increase in mean substance \overline{M} for the pulps treated with polyamine compared with the controls (PR-35, A-0, P-0). The mean substance for the control sheets is 60.4 g/m^2 and for the polyamine-treated sheets it is 62.6 g/m^2 . Although statistically the difference between the mean values is significant, further tests would have to be carried out to confirm this result. Such a difference could be explained as being due to flocculation of fines that become retained in the sheet. If the observed effect is true, then it is associated either with the change in polarity of Z.P. or with the coagulation of fines in the presence of polyamine, owing to a bridging action. The higher substance is unlikely to be connected with the magnitude of the Z.P.; otherwise, a high substance should also be observed in the alum series, which shows the lowest numerical Z.P.

A more sensitive test for the retention of fines would be to determine the solids content in the whitewater.

Ionic charge density and streaming charge density

Extensive studies of electrokinetic phenomena in fibrous pads have been carried out by Lewis⁽⁴⁵⁾ and Nammari⁽⁴⁸⁾ at Lehigh University. The most pertinent conclusions from these investigations in relation to the present study are—

- (a) The definition of the two important electrokinetic parameters—
 - (i) Electrokinetic charge density, which is defined as the ratio $\Delta p/V$ (e.s.u./ cm³) and described as 'apparent ionic charge density in the electrokinetically sensitive portion of the double layer'.⁽⁴⁹⁾
- (*ii*) Streaming charge density, which is defined as the ratio I/Q (e.s.u./cm³) which 'represents the number of ionic charges moved (or distorted at the double layer) by each cm³ of streaming liquid'.⁽⁴⁹⁾

(b) The derivation of a new stream current equation based on Helmholtz' double-layer theory and the Kozeny-Carman permeability equation. $^{(45)}$

The present experimental results have been used to evaluate electrokinetic charge density (E.C.D.) and streaming charge density (S.C.D.). In order to assess the effect of pad porosity on E.C.D. and S.C.D., the qualitative aspects of the equation proposed by Biefer & Mason (B-M) are compared with those for the equation proposed by Lewis & Nammari (L-N).

The two equations are compared in Table 4 within the framework of the

TABLE	4-STREAM	CURRENT	EOUATIONS
		CONCERNI	LQUITIOND

Generalised form		
Biefer-Mason	Lewis-Nammari	
$\frac{l}{\Delta p} = \frac{k}{L} \epsilon^{5/2}$	$\frac{l}{Q} = k \frac{L(1-\epsilon)^2}{\epsilon^3}$	

Experimental conditions

$\epsilon = (1 - ar{lpha}C) = 1 - rac{lpha W}{A L}$ Thereform	pre, $L = \frac{\alpha W}{A(1-\epsilon)}$			
$R_p = BL + D$ Therefore, $V = IR_p$	$I_{p} = I(BL+D) = I\left(\frac{B^{1}}{1-\epsilon}+D\right)$			
$Q \propto \Delta p rac{\epsilon^3}{(1-\epsilon)^2} \qquad \epsilon < 0.8 \; [{ m Ref.}^{~(46)}]$				
$\frac{\Delta p}{V} = \frac{1}{\epsilon^{5/2}[k_1 + k_2(1 - \epsilon)]} \qquad \qquad \frac{\Delta p}{V} = \frac{(1 - \epsilon)^2}{k_3 + k_4(1 - \epsilon)}$				
$\frac{l}{Q} = k_5 \frac{(1-\epsilon)^3}{\epsilon^{1/2}}$	$\frac{l}{Q} = k_6 \frac{(1-\epsilon)}{\epsilon^3}$			
Limiting conditions				
$\epsilon \rightarrow 0 \qquad \frac{\Delta p}{V} \rightarrow \infty$	$\epsilon \to 0 \qquad \frac{\Delta p}{V} \to \frac{1}{k_3 + k_4}$			
$\epsilon \rightarrow l$ $\frac{\Delta p}{V} \rightarrow \frac{1}{k_1}$	$\epsilon \rightarrow I \qquad \frac{\Delta p}{V} \rightarrow 0$			
$\epsilon ightarrow 0 \qquad \frac{l}{Q} ightarrow \infty$	$\epsilon ightarrow 0 \qquad \frac{l}{Q} ightarrow \infty$			
$\epsilon ightarrow I \qquad \frac{l}{Q} ightarrow 0$	$\epsilon \rightarrow 1 \qquad \frac{l}{Q} \rightarrow 0$			

present experiment, for example, by noting that pad length L is related to porosity ϵ and that pad resistance R_p is a linear function of pad length.

The experimental results are insufficiently sensitive to test the predicted and observed values of E.C.D. and S.C.D. in the range of porosities encountered in the experiments, therefore the comparisons of the two equations have been carried out by considering limiting conditions (Table 4). The L-N equation requires that E.C.D. should tend to zero as porosity tends to unity, whereas the limiting value of E.C.D. according to the B-M equation is a small quantity of the same sign as the E.C.D. values. The experimental results appear to be in keeping with the B-M requirement (Fig. 14 and 15).

At the other limit, there is little to distinguish between the two equations, even though there is no indication that E.C.D. tends to a limiting value as required by the L-N equation (Fig. 14 and 15).



Fig. 14—Graphs of electrokinetic charge density against reciprocal porosity for pulp pads treated with different concentrations of alum in the presence of $10^{-3}N$ sodium chloride

The simplest function to satisfy the limiting conditions of the B-M equation is—

$$\frac{\Delta p}{V} = \frac{C_1}{\epsilon} + C_2 \qquad . \qquad . \qquad . \qquad (13)$$

The experimental results were used to evaluate the regression constants C_1 and C_2 for the different pads. The experimental values and the calculated lines are shown in Fig. 14 and 15; the intercept and slope values are listed in Table 5.

The S.C.D. expressions have the same limits for both equations and the results for a number of pads in this case were evaluated in the form—

 $I/Q = f(\epsilon)$ $f(\epsilon) = K' \frac{(1-\epsilon)^3}{\sqrt{\epsilon}} \text{ for B-M equation}$ $f(\epsilon) = K'' \frac{(1-\epsilon)}{\epsilon^3} \text{ for L-N equation}$



Fig. 15—Graphs of electrokinetic charge density against reciprocal porosity for pulp pads treated with different concentrations of polyamine in the presence of 10^{-3} N sodium chloride

Pulp	$[\Delta p/V]\epsilon = 1,$	Slope constant,	$[I/Q]\epsilon = 0.6,$
	10 ¹⁰ e.s.u./cm ³	C_1	10 ⁴ e.s.u./cm ³
A-0 A-10 A-25 A-50 A-100 P-0 P-1 P-5 P-10 P-100 P-100 P-1000 10 ⁻⁴ N NaCl	$\begin{array}{r} -0.32 \\ -0.57 \\ -0.74 \\ -1.87 \\ -1.93 \\ -0.33 \\ +0.41 \\ +0.39 \\ +0.30 \\ +0.37 \\ +0.71 \\ 0 \end{array}$	$\begin{array}{r} -1.05 \\ -0.88 \\ -1.37 \\ -2.36 \\ -3.02 \\ -1.35 \\ +6.44 \\ +1.40 \\ +0.91 \\ +0.44 \\ +0.89 \\ -0.35 \end{array}$	$\begin{array}{r} -1.2 \text{ and } -1.4 \\ -1.1 \\ -0.7 \\ -0.3 \\ -0.2 \\ -1.3 \text{ and } -1.0 \\ +1.2 \\ +0.8 \\ +0.9 \\ +1.9 \\ +1.5 \\ -1.9 \end{array}$

TABLE 5—ELECTROKINETIC PARAMETERS $\Delta p/V$ AND I/Q

The purpose of these tests was to determine which expression yields a better linear function with S.C.D. and whether the intercepts are zero as required by the two equations. The results for three pads are shown in Fig. 16–18. As can be seen from the results, the intercepts may or may not be zero (depending on the pad) and the linear relationships fail at lower porosities for both equations. On the assumption that S.C.D. is a function of (ϵ) and $(1-\epsilon)$ with zero intercept of the form—

$$I/Q = a\epsilon^{b}(1-\epsilon)^{c} \qquad . \qquad . \qquad . \qquad (14)$$

the coefficients a, b and c were evaluated for three pads. The resultant equations are shown in Table 6 and the experimental values together with the calculated lines in Fig. 19.



Fig. 16—Graph of streaming charge density against porosity functions calculated from two stream current functions for a pad treated with 10^{-3} N sodium chloride

From the results in Table 6, it can be seen that the experimentally determined coefficients agree with neither of the proposed equations. In view of this, it is not practical to classify the pads in terms of S.C.D. at a limiting value of porosity, but they may be quoted for a specific porosity. The values for $\epsilon = 0.6$ are listed in Table 5.

Although the experimental values are not sensitive enough to prove or disprove either of the theories, an interesting point emerges with respect to the E.C.D. analysis. If the interpretation by Lewis & Meyer ⁽⁴⁹⁾ of the physical significance is correct, then, at the limiting value as $\epsilon \rightarrow 1$, the E.C.D. may be

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Fig. 17—Graph of streaming charge density against porosity functions calculated from two stream current functions for a pad treated with 25 ppm alum in the presence of 10^{-3} N sodium chloride



Fig. 18—Graph of streaming charge density against porosity functions calculated from two stream current functions for a pad treated with 100 ppm polyamine in the presence of 10^{-3} N sodium chloride

 TABLE 6—THE EFFECT OF POROSITY ON STREAMING CHARGE DENSITY

Pad identification	S.C.D., $10^4 e.s.u./cm^3$
10 ⁻⁴ N NaCl A-25 P-100	$ \begin{array}{l} I/Q = 0.414\epsilon^{-2.75}(1-\epsilon)^{0.15}\\ I/Q = 84.0\epsilon^{2.30}(1-\epsilon)^{3.93}\\ I/Q = 22.7\epsilon^{1.61}(1-\epsilon)^{4.30} \end{array} $

a measure of the ionic charge density (I.C.D.) in the double layer when the fibres are completely dispersed. The I.C.D. appears to be primarily controlled by the concentration of the electrolyte, since there is no significant change in I.C.D. between the four controls and the P-1 to P-1000 samples (other than change in polarity). Furthermore, the value of I.C.D. decreases with decreasing ion concentration $(10^{-4}N \text{ sodium chloride solution})$ and increases with increasing alum concentration (Table 5).



Fig. 19—Graph of streaming charge density against porosity for the pads of Fig. 16–18

The odd result for the P-1000 pad is possibly due to the fact that the polyamine is contaminated with some inorganic material (shown in an ash test) and that this produces the increased I.C.D. The increase becomes significant at high polyamine concentrations.

It is of interest to note that the I.C.D. for the controls is about 3×10^9 e.s.u./cm³, which is ten times higher than the charge density in the rest of the electrolyte (0.3×10^9 e.s.u./cm³ for 10^{-3} N sodium chloride solution).

Conclusions from the electrokinetic study of fibre/water interfaces

On combining the information from the Z.P. and I.C.D. studies, it is apparent that in terms of equation (12) the action of polyamine is to reverse the charge on the fibres and that subsequent increases in Z.P. with increasing polyamine concentration are due to increased charge. At very high polyamine concentrations, the Z.P. values are slightly reduced by the presence of ionic impurities. The action of alum is primarily that of an electrolyte as indicated by the increase in I.C.D. with increasing alum concentration.

In the present study, the evaluation of E.C.D. and subsequently I.C.D. helped in determining the relative contributions of charge and ion concentration to the zeta-potential, therefore the I.C.D. may prove a useful addition parameter for the study of electrokinetic properties of fibre/water interfaces.

Consolidation

General

In order to understand the effect of non-fibrous materials on consolidation of the paper web, it is insufficient to take into account the empirical effects on concentration and cohesion of the structure at the various stages of deposition, drainage, pressing, drying and calendering. Ultimately, the explanation of effects of practical value lies at the molecular, microfibrillar or fibre level. Thus, it will be of greater profit to examine phenomena such as fibre collapse, surface tension and hydrogen bonding in relation to the physical and chemical properties of particular non-fibrous materials.

Surface tension

On the theory put forward by Campbell⁽⁵⁰⁾ in 1933, surface tension forces would be expected to operate throughout the three-phase stage of the formation process—that is, from the dry line on a papermachine to the point in the dryers at which the free water has been eliminated (excluding the presses, where the water is squeezed temporarily to the surface of the web). The fibres or attached fibrils are regarded as being pulled into intimate contact as a preliminary to the development of interfibre bonds. The manner in which these forces are thought to operate was summarised by Swanson⁽³⁾ on the basis of the early ideas of Campbell⁽⁵⁰⁾ and more recent studies by Lyne & Gallay,⁽⁵¹⁾ pertaining particularly to wet web strength.

Experimental evidence that has been advanced or invoked to support Campbell's theory includes the low strength of freeze-dried paper,⁽⁵²⁾ of paper dried by solvent exchange⁽⁵³⁾ and of paper formed in the presence of surfactants.⁽⁵⁴⁾ The freeze-drying and solvent exchange experiments cannot be interpreted entirely in terms of the Campbell effect, however, since these processes not only reduce the effect of surface tension, but also lead to immobilisation of the polysaccharide chains, thus preventing hydroxyl groups from coming into the most favourable positions for interchain and interfibre hydrogen bonding. Touchette & Jenness⁽⁸⁾ found that in general the strength reduction brought about by surfactants was markedly influenced by the type of surfactant and was considerably increased as the potentialities for adsorption of surfactant on to the surface of the fibre increase (in the order anionic, non-ionic, cationic type of surfactant).

The influence of anionic surfactants on consolidation appears to vary according to the extent of wet pressing. Lyne & Gallay⁽⁵⁴⁾ found that, with paper that had been given a minimum amount of wet pressing, the presence of an anionic surfactant caused considerable reduction in both wet and dry strength, which must be attributed to surface tension effects. With normally pressed sheets, Touchette & Jenness⁽⁸⁾ found little change in strength. It therefore seemed to be of interest to investigate, with comparable material, the relative effects of wet pressing and surface tension on consolidation as assessed by mechanical behaviour. A further indication that under some circumstances surface tension forces do not play a major role in the formation of interfibre bonds is the observation⁽⁵³⁾ that solvent-dried papers of low strength are able to attain strengths equal to those of normally dried papers from similar pulps, if exposed to atmospheres above 85 per cent relative humidity. A related phenomenon has been observed in this laboratory in that the elastic modulus of paper on stress/strain cycling is reduced at relative humidity below 50 per cent, but is increased above 65 per cent. This may be partly a consequence of the ability of hydrogen bonds to reform, if the moisture content is sufficiently high, even without the intervention of liquid water.

In the present experiment, handsheets were prepared in the following ways from both long-fibred and short-fibred pulps, with and without an anionic surfactant—

Unpressed, dried normally (under restraint) Pressed, dried normally (under restraint) Pressed, dried free of restraint on polythene sheeting.

Normal sheetmaking techniques were followed, except as required to obtain the appropriate variable. In addition, as it was necessary to form the unpressed sheets in such a manner that they could be removed from the sheetmachine without couch rolling, all sheets were formed on a piece of Terylene voile laid flat on top of the normal wire and held in place by the clamping pressure of the sheetmachine. This made it possible for the unpressed sheets to be lifted from the wire and placed on a drying plate between the drying rings without any application of couching pressure. The only forces that could be involved in the compaction of the sheet were therefore drainage forces and surface tension forces.

The effects of the various treatments on the following properties were studied— sheet strength properties, wet tenacity, drying tensions measured as described previously⁽⁵⁵⁾ and the load/deformation curves of strips dried in the normal way. The results obtained were rather complex, but it was clear that

TABLE 7—EFFECT OF WET PRESSING AND DRYING UNDER RESTRAINT ON THE OPERATION OF SURFACE TENSION FORCES

The following abbreviations are used throughout-

Euc.	Eucalypt kraft pulp
Pine	Long-fibred kraft pulp, mainly pine
W_1	Substance 60 g/m ²
$\overline{W_2}$	Substance 120 g/m^2
$\tilde{B_0}$	Unbeaten
$\tilde{B_1}$	Beaten 4 500 rev Lampén mill (euc.) or 200 rev PFI mill (pine)
B_2	Beaten 18 000 rev Lampén mill (euc.) or 700 rev PFI mill (pine)
$\overline{C_0}$	No anionic surfactant added
C'_1	10 ml anionic surfactant to stock divider
C_1	10 ml anionic surfactant in sheetmachine
R_0	Dried without restraint
R_1	Dried with restraint
P_0^-	Unpressed
P_1	Wet pressed after formation of sheet
M_1	69 per cent moisture content
M_2	40 per cent moisture content
Double lines	Difference significant at 0.1 per cent level
Single line	Difference significant at 1 per cent level
Broken line	Difference significant at 5 per cent level

TABLE 7*a*—Euc, B_1 , W_2

Two experiments, in which treatments C_0 , C'_1 and C_0 , C_1 were adopted, showed no differences in controls for the properties shown below nor could significant differences be detected between sheets treated at the two levels of surfactant used. The two experiments were therefore combined to yield the following results-

	Tenacity*		
	P_1		
	R_0	R_1	
C_0	21.4	25.3	
<i>C</i> ₁	22.7	25.5	

Slope*							
<i>P</i> ₁							
R_0 R_1							
5.84	10.9						
7.85	10.5						

Extensibility*							
<i>P</i> ₁							
9.25	4.01						
6.55	5.18						

* Arbitrary units from load/deformation curves

	Tenacity*							
	$P_0 P_1$							
	R	1	R ₀					
$\overline{C_0}$	9.93	13.7	10.9					
$\overline{C_1}$	5.16	12.9	9.80					

TABLE 7 <i>b</i> —Euc., B_1 ,	W_1
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Slope*					
P_0 F	P ₁				
<i>R</i> ₁	R_0				
4.30 4.37	3.04				
2.70 4.18	3.06				

Extensibility*‡								
P_0	P_1		P_1					
R_1	R_0		R_1					
4.06	7.70		6.14					
2.44	6.48		5.44					

* Arbitrary units from load/deformation curves ‡ Extensibility results could not be combined for all treatments, because variance was a function of treatment

TABLE 7c—Euc., B_1 , W_1

Caliper, burst, tensile, tear and stretch are adjusted for substance

		Fold		Air	Air resistance			Tear				Tensile				
	P_0	P_0 P_1		P_0	P_0 P_1		P_0 P_1			P_0	P	1		P_0	l	P ₁
	R	$R_1 \mid R_0$		I	R_1 R_0		R_1 R_0		1	R_1		R_0		R ₁		R_0
$\overline{C_0}$	11.5	52.1	39.9	0.82	0.82 9.6 9.8			79.5 105 96.0			4.65 7.42 6.2		6.22			
$\overline{C_1}$	1.62	57.0	31.2	0.42	0.42 7.4 7.0			46.6	93.6	89.5		2.67	7.44	6.17		
	<u></u>		<u> </u>	<u>k</u>	U		4			-			<u></u>			
	Stretch			Burst			Caliper			Moisture						
	Po	P	2	P_{0}	1	P ₁		P_0	P	1		P_0	ŀ	P ₁		

	Γ_0	1	1						
	R	R_1							
$\overline{C_0}$	2.10	2.50	4.62						
$\overline{C_1}$	1.22	2.88	4.56						
		1 I							

Burst									
P ₀	P_0 I								
R	R_1								
26.1	26.1 43.0								
10.0	44.6	44.4							

Caliper								
P_0 P_1								
R	R_1							
2.88	2.88 1.56							
3.74	1.59	1.76						

Moisture									
P_0 P_1									
R	R_0								
11.32	11.32 10.86								
11.32	11.16	10.58							

TABLE 7d— W_1 , P_1 , R_1

Caliper, burst, tensile, tear and stretch are adjusted for substance

	Euc. Fold		P F	ine old	resi	Euc. Air resistance		Pine Air resistance		Euc. Tear		Pine Tear	
	<i>B</i> ₁		B ₁		B_1	B ₂	B_1		B_1	B_2	B_1		
$\overline{C_0}$	52.1	498	900	3280	9.6	110	2.9	340	105	96.5	156	105	
$\overline{C_1}$	57.0	355	1090	2030	7.4	54	3.9	66	93.6	96.9	153	116	

	Ει	ıc.	Pi	ne	Ei	uc.	Pi	ine	Eı	ıc.	Pi	ine
	Ten	sile	Ten	sile	Str	etch	Str	etch	Bu	vrst	Bu	ırst
	B ₁	B_2	<i>B</i> ₁	B ₂	B ₁		<i>B</i> ₁		B_1	B_2	<i>B</i> ₁	
$\overline{C_0}$	7.42	9.29	6.38	10.2	2.50	3.18	3.04	4.56	43.0	67.1	54.3	83.3
$\overline{C_1}$	7.44	9.64	6.73	9.62	2.88	3.62	3.34	4.12	44.6	66.0	53.8	78.3

	Euc.	Euc.	Pine	Pine	Eu	с.	Pi	ine
	Cali- per*	Cali- per*	Cali- per*	Cali- per*	1	Moisture	e conten	t
	<i>B</i> ₁	B_2	<i>B</i> ₁	B ₂	B ₁	B_2	B ₁	B ₂
C_0	1.56	1.38	1.71	1.44	10.86	9.62	10.59	10.74
C_1	1.59	1.43	1.68	1.49	11.16	9.56	10.30	10.97

* Caliper results could not be combined, because variances were found to be a function of treatment

Wet tenacity*							
M	ſ ₁	A	12				
B ₀	<i>B</i> ₁	B ₀	<i>B</i> ₁				
1.36	1.48	3.60	3.60				
0.94	1.36	2.88	3.38				

TABLE 7e-Euc., W1, P1

* Arbitrary units

TABLE 7*f*—Euc., W_1 , B_1 : INDIVIDUAL STRIPS DRIED FROM M_1 , UNDER 100 g LOAD, THEN LOAD/DEFORMATION CURVES MEASURED

_	Tenacity*	Slope*	Extensibility*
Co	9.4	2.71	8.0
$\overline{C_1}$	10	2.97	7.9

* Arbitrary units from curves

Insufficient samples to determine significance of difference in means for C_0 and C_1

most of the properties usually associated with interfibre bonding were not affected significantly when the sheets were wet pressed. Nevertheless, highly significant effects were observed in the absence of wet pressing as shown in Tables 7b and 7c for tenacity, initial slope of the load/deformation curve, extensibility, folding endurance, tear, Schopper tensile, stretch, burst and caliper. Air resistance, stretch and caliper were also affected when the sheets were wet pressed as shown in Table 7d.

These results, which are in accord with the work of both Lyne & Gallay⁽⁵⁴⁾ and Touchette & Jenness,⁽⁸⁾ demonstrate the importance of surface tension

as a compacting force in the absence of external pressure on the wet web, at least in the stage at which the air/water interface is drawn through the fibre pad.^(3, 9, 50) There are indications that the effect of surface tension may be overshadowed to a large extent by the effect of pressing; yet, even if this were to be found to apply generally, the surface tension forces could still play an important role in consolidation at the wet end by providing wet strength at the couch and in the press (see Table 7*e*).

The magnitude of the decrease in thickness of the fibre web as water is replaced by air is very considerable. In the course of experiments described in another contribution to this symposium,⁽⁵⁶⁾ the decrease in thickness of various pulp pads was measured. The decrease as a percentage of the final thickness was as follows for a series of *P. radiata* sulphate pulps⁽⁵⁷⁾ at various stages of bleaching—

Lignin, per cent	4.6	2.4	1.7	1.1	0
Thickness decrease	97	90	96	111	125
(per cent of final					
thickness)					

Corresponding values for *E. regnans* neutral sulphite semi-chemical pulps cooked to various extents⁽⁵⁸⁾ were as follows—

Lignin, per cent	12.9	10.7	6.9
Thickness decrease	36	38	44
(per cent of final			
thickness)			

The two series are not comparable, as the pads were subjected to different loading histories, but the treatments within each series were the same. The results suggest that more flexible fibres, at the lower lignin contents, can be drawn into closer contact as air enters the pad.

Fibre properties

In view of the significance of fibre flexibility on papermaking properties and of the role of fibre collapse in increasing the bonded area of the sheet, it is pertinent to enquire what effects non-fibrous additives are likely to exert on the mechanical properties of the fibre. With this aim in view, an attempt has been made to develop a method of examining the behaviour of individual fibres in lateral compression. The fibre is placed on a glass slide and viewed obliquely with a microscope; at the same time, it is loaded directly by the probe of a thickness gauge. Different loads can be applied by means of a spring loading device (calibrated independently) and the deformations measured on the gauge. The end of the probe is flat and of about the same diameter as the width of the 'ribbon' of a collapsed fibre. (*P. radiata* fibres were used in this work.) Loads up to 100 g were applied and measured, the corresponding pressure range being up to 1.7×10^6 g/cm².

Load/compression curves were plotted for fibres air-dried from water (collapsed), dried from ethanol and ether (not collapsed) and in the wet (never-dried) state (Fig. 20).



Fig. 20—Load/deformation curves for individual fibres in lateral compression

The deformation of the fibres can be interpreted in terms of the closing of the lumen and the consequent compression of the wall material. To assist in interpretation of the load/compression curves, some model tests were carried out on various tubular structures; in Fig. 21 curves are shown for a stiff thinwalled cardboard tube subject to elastic deformation and crushing and for thin-walled and thick-walled rubber tubes in which the closing of the 'lumen' is and is not, respectively, a major factor in deformation. The crushing of a tube between rigid plates has been discussed by De Runtz & Hodge,⁽⁵⁹⁾ who have observed sigmoid curves similar to those shown in Fig. 21, the influence of geometrical changes after initial yield resulting in increased load-carrying capacity. The analogies with lateral fibre compression are evident and it can be seen that, with the partially collapsed fibre dried from water, the portion of the curve reflecting lumen closure is greatly foreshortened compared with that for the solvent-dried fibre. The additional inflections in the curve for the

4—с.р.w. п

uncollapsed fibre may well be a real effect, resulting from the fact that the lumen first closes at the centre of the ribbon, leaving two sub-lumens, which are then subjected to deformation as before. The load/deformation and recovery curves are modified by crushing of the wall material, which must take place at the high pressures involved.

This technique has not yet been used to a great extent to assess the effect of additives. A comparison was made between the fibres of a klinki pine sulphate pulp before and after treatment with cationic starch; but, from the limited number of tests made, no definite conclusions could be drawn. Clearly, any



Fig. 21—Load/deformation curves in lateral compression for tubes of different wall thickness and elastic modulus

such studies must be on a statistical basis and, in the context of consolidation mechanism, they should be carried out on the wet fibres. Small samples of the two groups of fibres were also tested dry in tension in the DFP single fibre rheometer⁽⁶⁰⁾ and the numbers of fibres falling in the load ranges (g) 0–5, 5–10, 10–20, 20–30, 30+ were respectively, for the untreated and starch-treated pulps, 4, 12, 1, 1, 2 and 2, 5, 4, 3, 6. These figures lend some support to the possibility of starch reinforcement of the fibres.

Sheet thickness and density

The density of the sheet is a good reflection of the lateral conformability of the individual fibres, it has a very considerable influence on the mechanical properties of the paper and it has the advantage of being easily measured. Hence, the effect of additives on consolidation can be assessed by this property and a considerable body of information of this kind is available in the literature. The additives that might affect the response of the wet mat to compression are, in the main, those that affect the mechanical properties of the wet fibre. Relative movement of the fibres does contribute to compressibility,^(56, 61) although this effect becomes less as the fibres become more flexible by delignification⁽⁵⁶⁾—probably, also by beating—and it is conceivable that some additives may have a lubricating action that favours repositioning of the fibres. Yet the stiffer fibres that show the greatest relative movement during compression eventually form the bulkier sheets, so it appears that the compressibility of the fibres themselves is the main factor in the degree of consolidation attained in the end.

In order to affect the behaviour of the fibre in compression, an additive must be able to penetrate the amorphous regions. This is likely to occur only with small molecules or ions. Alum is perhaps the most common beater additive that may fulfil these conditions; the trivalent aluminium ion should be able to penetrate the gel structure. The behaviour of negative gels in the presence of polyvalent cations is well known and the detailed studies of Cohen, Farrant & Watson⁽⁶²⁾ on the influence of cations and anions on pulp and paper properties showed that trivalent and tetravalent cations produce a marked increase in bulk. This must involve a contraction of the gel structure and a corresponding decrease in lateral conformability. Swelling agents give rise to an increase in conformability and a corresponding decrease in bulk.

After the pressure on the wet sheet has been released, the mat tends to increase in thickness, as a consequence of the elastic energy stored in the fibres. This tendency will be opposed by any incipient interfibre bonding and by surface tension forces, both of which factors will be influenced by the amount of water that has been removed. Thus, the presence of any additive that alters bonding capacity, surface tension or moisture content could affect the final sheet thickness. For example, as shown by Watson,⁽⁶³⁾ the presence of an adsorbed dyestuff (Congo red) on the surface of an unbeaten eucalypt sulphate pulp inhibits interfibre bonding and leads to an increase in bulk from 1.85 to 2.02. It is to be anticipated that any adsorbed material not able to form interfibre bonds will behave in a similar manner. Such materials include nonionic and cationic surfactants, mineral fillers and hydrophobic colloids such as rubber latices. Conversely, the increased interfibre bonding brought about

by guar gum increases sheet $density^{(64)}$ and a slight increase in density has been noted in the presence of starch.⁽⁶⁵⁾

Mechanical properties of paper

The effect of additives on the mechanical properties of paper may be considered briefly according to the classification of non-fibrous materials given earlier and in terms of their effect on interfibre bonding. The hydrogen bond concept of paper strength is now generally accepted as discussed elsewhere,⁽⁶⁶⁾ although controversy persists on the manner in which the molecular interactions are influenced by fibre morphology⁽⁶⁷⁾ and on the extent to which molecular models are appropriate to a material possessing a complex supermolecular structure.^(68–70) Much of the argument about the relationship between fibre properties and density applies also to paper strength. The following general concepts about the various categories of non-fibrous materials can now be enunciated—

- (i) Colloids present in the regions of interfibre contact will modify the interfibre bonding in a manner dependent on the characteristics of the cellulose/ colloid interface as discussed below.
- (ii) Surfactants, if capable of being adsorbed, will behave in a way similar to other small molecules—see (iv); in addition, the reduction in surface tension will reduce the forces holding together the fibres in a wet mat, which may under some circumstances affect the dry strength.
- (*iii*) Electrolytes are able to penetrate the fibre and may affect the physical properties of the fibre and its electrokinetic behaviour.
- (*iv*) Other non-polymeric materials may be adsorbed at the fibre surface and hinder the surface hydroxyl groups from forming interfibre hydrogen bonds, but may provide instead different bonding properties according to their own chemical nature.

Effect of starch and other colloids

From results obtained in the study of various modified starches and starch fractions as beater additives, it has been concluded that three factors influence the interfibre bond—the state of dispersion of the colloidal material, the internal cohesion of the dried colloid film and the strength of adhesion at the colloid/fibre interface.

The state of dispersion of starch can be varied by cooking at different temperatures and the effect of dispersion on bonding properties is shown in Table 8. The state of dispersion of the colloid controls its surface-covering capacity, also its ability to flow under pressure so as to fill in the irregularities within the contact area; cohesion and adhesion of the dried film will be related to the nature of failure and the force required to bring it about.

Non-fibrous materials and flocculation

Although starch is the only colloid we have studied in this context,^(65,71) it is probable that this type of approach can lead to an assessment of the effect of any colloidal material on interfibre bonding, provided the colloid is retained in the sheet by adsorption, not by mechanical retention.

The basic factors influencing the effects brought about at various states of dispersion are particle size and plastic flow properties. Additives such as fillers and pigments that do not flow easily under pressure may give rise to discontinuities within the bonded area, which would reduce interfibre bond strength. Smaller particles will tend to increase coverage of the fibre surface at a given level of retention, thus to enhance the effect of the additive, whether

TABLE 8--INCREASE IN BURST FACTOR AND LOG FOLDING ENDURANCE AT 0.5 PER CENT STARCH RETENTION

Pulp and	Beating,	S	Starch cooking temperature, °C				
property	rev PFI	65	75	85	100		
Pine Bursting strength (increase)	0 2 000 5 000 7 000	13 22 8 4	16 24 10 5	19 26 14 4	21 28 15 8		
Eucalypt Bursting strength (increase)	0 1 125 4 500 18 000	5 10 9 5	8 11 12 12	8 13 16 12	8 16 20 13		
Pine Log fold (increase)	0 2 000 5 000 7 000	0.8 0.25 0.05 0.05	1.2 0.25 0.05 0.05	1.2 0.35 0.15 0.05	1.1 0.40 0.20 0		
Eucalypt Log fold (increase)	0 1 125 4 500 18 000	0.35 0.25 0.25 0.10	0.50 0.35 0.60 0.15	0.60 0.35 0.65 0.35	0.55 0.45 0.75 0.30		

(Sulphate pulps: cationic starch, values obtained by interpolation on beating curves)

advantageous or not. The ability to flow easily will also enhance the surface coverage.

In an attempt to determine more clearly the factors responsible for additive efficiency, the effect of chemical modification on the behaviour of wheat starch has been investigated.⁽⁷¹⁾ In order to eliminate variables introduced by the presence of retention aids, the papermaking fibre was converted to a tertiary alkylamino ether, on to which the starches and modified starches were directly adsorbed. The starches used included native wheat starch, its component amylose and amylopectin fractions and the products obtained from it by

acid hydrolysis, bromine and hypochlorite oxidation, hydroxyethylation and carboxymethylation. The adhesive properties at the starch/cellulose interface were evaluated by measuring the peeling force with cellulose tape as the adherend and the appropriate starch as adhesive by means of a simple device described elsewhere.⁽⁷²⁾

Some of the results of this work are shown in Tables 9 and 10. Hetero-

 TABLE 9—INCREASE IN PAPER STRENGTH (BURST FACTOR AND BREAKING LENGTH IN km) AT 0.5 PER CENT STARCH RETENTION

 (Long-fibred kraft pulp converted to tertiary alkylamino ether before starch adsorption

	Conditions of modification							
Starch modification	Light		Moderate		Severe			
·	Bursting strength (increase)	Breaking length (increase)	Bursting strength (increase)	Breaking length (increase)	Bursting strength (increase)	Breaking length (increase)		
Acid hydrolysis Hydroxyethylation Carboxymethylation Bromine oxidation Hypochlorite oxidation	10.5 9.0 6.5 8.5 5.0	0.90 0.65 0.70 0.85 0.60	9.0 8.5 2.5	0.80 0.65 0.40	8.5 8.0 7.0 3.5 1.5	0.80 0.75 0.60 0.50 0.45		
Unmodified	Bursting	strength ir	crease 4.5	Tensile st	rength inci	ease 0.60		

geneous acid hydrolysis and mild bromine oxidation yield starches that give increased bursting and tensile strengths compared with unmodified starch; hydroxyethylated and carboxymethylated starches give increased burst, but the same increase in tensile strength. Severe oxidation either with bromine or with sodium hypochlorite reduces both burst and tensile improvement.

These results suggest that the improvement in starch dispersion characteristics brought about by chemical modification is advantageous, unless the film strength (which is a measure of the internal cohesion of the starch film) is reduced at the same time, which occurs primarily in the severe oxidation treatments. Amylopectin, however, which has a lower film strength than

 TABLE 10—EFFECT OF STARCH FRACTIONS ON INCREASE IN PAPER STRENGTH AT 0.5 PER CENT RETENTION AND ADHESION AT CELLULOSE/STARCH INTERFACE

 (Pulp as in Table 9)

Starch	Increase in breaking length, km	Increase in burst factor	Peeling force (arbitrary units)
Native wheat	0.85	10.0	3
Wheat amylose	0.95	8.0	5
Wheat amylopectin	1.20	14.0	15

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Non-fibrous materials and flocculation

amylose, has been reported by a number of workers to be much more effective as a beater additive, despite the fact that both can be prepared as dispersions of virtually molecular dimensions. An explanation of the phenomenon was sought in the adhesive characteristics of the two starch fractions.

The measurements of peeling force (Table 10) showed that the adhesion of amylose to cellulose was much less than that of unfractionated starch, which was similar to acid-hydrolysed starch and slightly less than the amylopectin fraction. Comparison of the starch fractions and the untreated starch as beater additives showed that amylopectin gave papers with better bursting and tensile strengths than did the unfractionated starch, whereas amylose gave papers with lower bursting strength, but similar tensile strength.

These results confirmed the view that dispersion, internal cohesion and adhesion at the fibre/colloid interface all contribute to the effect of additives on interfibre bonding, but the emphasis to be put on one or another of these mechanisms depends on the type of material. For hydrophobic colloids such as natural and synthetic latex emulsions (probably to some extent for resins and sizes), adhesion is likely to be the controlling factor. The requirements for good adhesion in polymeric colloids may be set out on the basis of Voyutskii's diffusion theory of adhesion,⁽⁷³⁾ which requires that the degree of polymerisation of the adhesive should be neither very high nor very low, that chain segments should be able to exhibit micro-Brownian movement while adhesion is occurring (the polymer should be in the plastic, not the glassy state) and that the adhesive and the adherend should exhibit some degree of mutual solubility. When these criteria are not met, adhesion may still take place by Van der Waals' sorption forces or by electrostatic attraction, but such associations between consolidated bodies are not likely to be strong.

Acknowledgements

The authors are grateful for willing help rendered by various colleagues: Miss Nell Ditchburne of the CSIRO Division of Mathematical Statistics for analysis of the flocculation data, Mr J. de Yong for advice and assistance in connection with the zeta-potential apparatus, Mr L. N. Clarke and Mr N. Edwards for electrical work on the beta-ray scanner and the zeta-potential apparatus, Miss Janet Ward and Mr R. McNamee for assistance in the experimental work, Mr F. Peplar for construction of the beta-ray scanning device. We should like also to thank the Australian Atomic Energy Commission for the loan of equipment used in connection with the flocculation experiments.

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Discussion

Mr G. Jacquelin—My first point deals with an experimental detail for zetapotential measurement. In a paper published last year,⁽¹⁾ we pointed out that the system consisting of two silver/silver chloride electrodes with a fibre plug between them had photoelectrical properties and that it was necessary for reliable results to enclose the cell in an opaque box. Have you noticed such effects for the measurements reported in your paper?

My second point deals with the action of hydrophilic colloids on flocculation. Fig. G, H, J & $K^{(2, 3)}$ make clear the fact that a given additive may be flocculating, deflocculating or without action, the effect being conditioned by the composition of the liquid medium.

In these graphs, we have plotted the relative variations of a flocculation index of the flowing suspension, measured by means of an optical device that has been described elsewhere.⁽⁴⁾

Fig. G shows the action of various carboxymethylcelluloses on flocculation for a bleached hardwood pulp suspension. When sulphuric acid is added to bring the pH value down to 4.5, the deflocculating effect disappears, in spite of the fact that the CMC retention on the fibres improves in acid medium. Addition of aluminium sulphate also greatly modifies the effect of CMC on flocculation (Fig. H, J & K), even though CMC retention is also increased by aluminium sulphate. These observations emphasised the fact that, to understand the action of additives on sheet formation and consequently on network consolidation, we have to consider not only the quantity of the additives adsorbed on the fibres, but also the form in which they are adsorbed and the interference with the other components of the papermaking suspensions.

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Dr H. G. Higgins—I have no information on this effect. Certainly, Balodis has had considerable difficulty in obtaining stable readings. We have not carried out the observations in the dark.



Fig. G—Effect of different carboxymethylcelluloses on the flocculation index of beech pulp (3 g/litre) at different pH values



Fig. H—Changes in flocculation of beech pulp (3 g/litre) brought about by successive additions of CMC and alum



Fig. J—Changes in flocculation of beech pulp (3 g/litre) brought about by successive additions of alum and CMC



Fig. *K*—Changes in the flocculation index of beech pulp (3 g/litre) caused by fractional additions of alum and CMC

Mr L. Nordman—I can confirm your observations. We did not get a positive value and therefore had to choose an arbitrary value.

Prof. B. Steenberg—The magnitude of the forces of interaction between fibres in dilute and concentrated suspensions is very different indeed and therefore results obtained in dilute systems (for example, in the handsheet machine) may not be at all applicable to more concentrated systems such as are encountered in papermachine head boxes and on the machine wire. We have found that deflocculants used commercially and known to be fairly effective on papermachines, yet ineffective in handsheet machines, do not change the mechanical properties of fibre networks as measured in the elasto-viscometer. We have little data at present, but further work might indicate a way of investigating effects of deflocculants on, say, the fibre-to-fibre interactions at concentrations used commercially.

Chairman—I agree that most of the experiments carried out in the laboratory on the effect of additives on flocculation have in fact been done at low concentrations (less than 0.1 per cent), so your observations are quite valid. Jacquelin's work, however, has been at higher concentrations, about 0.3 per cent.

Dr Higgins—We are in agreement with what Steenberg has said. We started with handsheets, but are now proceeding to a study of machine-made papers. In examining flocculation in handsheets, one runs into many other difficulties as described in the paper. I am grateful for this reminder that the geostrophic effect in Melbourne is in the opposite sense to that experienced here, so we have another source of variability.

Mr Jacquelin—The pulp consistency used for our studies of the action of additives on the flocculation of flowing suspensions was sometimes as high as 3 g/litre. This is a maximum, because the pulp absorbs much of the light and the sensitivity is poor.

Dr F. A. Shabi—I am rather mystified by the trend variations in substance shown by Fig. 4–6. In addition to the small variations caused by flocculation, there appears to be additional variation superimposed over a distance of 3–4 cm. Can you throw some light on this matter?

Dr Higgins—We have been surprised at the magnitude of the substance variations, which I suppose is a function of the size of the aperture. In addition, systematic variation has been obtained as described in the paper. I would

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like to know if other people who have been doing beta-ray scans with a small aperture have observed similar effects.

Dr H. K. Corte—Did you use a continuous scan (I notice that the opening is about 3.1 mm^2) or was the scan step-wise, in which case the curves are smoothed out?

Dr Higgins-It was done in various ways. I think these curves are step-wise.

Dr E. L. Back—The wavelength of these flocs was questioned. I can confirm that for hardboards produced from a 1-2 per cent consistency stock, the average size of floc is the same, about 1 cm^2 .

I wish to stress a note sounded by Higgins on the lack of correlation between the zeta-potential and the degree of flocculation (page 644). Most of the fibres have too small a specific surface to show a real zeta-potential effect, but the effect is true for the fines. He proposes to investigate the whitewater instead. In work on charge effects for pitch control, we found whitewater analysis for fines to be a powerful tool.