Water-Soluble Polymers as Retention Aids in a Model Papermaking System. I. Polyacrylamides

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Synopsis

A series of polyacrylamides covering a wide molecular weight range were synthesized and employed as retention aids in a model papermaking system of cellulose fibers and titanium dioxide. The ability of the polymer to increase the proportion of added titanium dioxide that is retained in the formed paper sheet is strongly dependent on molecular weight, but not on pH. Adsorption isotherms on both pigment and fibers are strongly molecular weight dependent. Polyacrylamides have no more than a weak flocculating effect on fiber suspensions and stabilize dispersions of titanium dioxide. However, with mixed dispersions of fibers and pigment, in the same ratio (10:1) as in paper formation, strong coflocculation is evidenced by the higher molecular weight polyacrylamides. In this model system pigment retention is a consequence of a heteroflocculation by adsorbed polymer bridging between the particles of titanium dioxide and cellulose fibers, possibly augmented by improved filtration in the forming sheet. Electrostatic effects appear to be unimportant in the system under study.

INTRODUCTION

In papermaking, the solids pass as a dilute aqueous suspension to a fine mesh through which most of the water and some of the smaller particles escape during drainage while the rest form a sheet which, after drying and consolidation, becomes the paper. The mesh may be stationary as in a laboratory hand-sheet machine such as that used in the present study, but is moving in industrial paper machines. Retention is defined as the fraction of applied solids which are retained in the final paper sheet. The cellulose and the other solids, variously described as loadings, fillers, or pigments, should be retained to the maximum extent consistent with requirements of sheet uniformity and high opacity. Water-soluble polymers are commonly added to papermaking stock to improve the retention of fiber fines and pigments. Only low levels of polymer are required, typically of the order of 1 lb polymer to 1 ton (dry weight) of papermaking fiber. Such retention aids may also impart subsidiary benefits to the total papermaking process, in particular by improvement of effluent quality, although increased drainage rates, greater wet-strengths, and reduced "two-sidedness" are often claimed.[1]

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Much previous work on polymeric retention aids, which has been reviewed by Calver and Avery,[1] has concentrated on practical papermaking systems, that is to say, systems including alum and often other additives. For instance, Iliescu and co-workers[2] studied polyacrylamides as retention aids for kaolin-filled sulfite pulp in the presence of alum and concluded that the best efficiency was obtained with nonionic polymers of high molecular weight ($>10^6$). It is generally agreed that the retention mechanism commences before the pulp suspension is run on to the machine wire[3] and, according to Reynolds and Ryan,[4] a high molecular weight polyacrylamide, since it does not flocculate fibers alone, functions by agglomerating the mineral particles which are then better retained in the forming fiber pad. Perehal'skii and Makushina[5] have also investigated kaolin retention in alum-containing sulfite pulp suspensions and suggest that very high molecular weights ($>2.2 \times 10^6$) are necessary. In the model system of microcrystalline cellulose and some cationic polymers (Ionenes), Sandell and Luner[6] conclude that particle flocculation is entirely by charge destabilization, whereas Chang and Robertson,[7] working with another cationic polymer and a dispersion of cellulose fibers, consider that higher molecular weight species initially flocculate by a bridging mechanism, but that under shear conditions the configuration of adsorbed polymer may alter and that the cellulose surface charge is reduced, thus favoring an electrostatic mechanism for flocculation.

To obtain an insight into the mechanism of retention, it is advantageous to work with a model system; and in the present case, the addition of linear polyacrylamides to aqueous, mixed dispersions of cellulose fibers and titanium dioxide particles has been studied. The retention of the titanium dioxide in a single pass of the dispersion through a standard wire mesh is taken as the criterion for judging the efficiency of the added polymer. Overall retention in industrial practice, where the material passing through the mesh is recycled, will necessarily be greater than the single pass value. A prime objective was to investigate the relation between retention efficiency and the molecular size of the polyacrylamide; parallel studies of polymer adsorption and flocculation behavior have also been made. Subsidiary measurements reported include that of the sheet opacity: relatively expensive fillers such as titanium dioxide are used to make papers of high diffuse reflectivity, and retention of the pigment *per se* is valueless if the optical properties become worsened by particle agglomeration.

EXPERIMENTAL

Polymer Synthesis and Characterization

Acrylamide (B.D.H) was recrystallized twice from pure ethyl acetate and dried *in vacuo* at room temperature. Ammonium persulfate and sodium metabisulfite (B.D.H) for redox initiation were used as supplied. Distilled water was deionized to a specific conductivity of ca. 5×10^{-7} ohm^{-1} cm^{-1} and then boiled and recooled at room temperature in a stream of oxygen-free nitrogen. Polymerization of 5% (w/v) monomer solutions was carried out at room temperature for 48 hr before precipitation of the polymer with methanol; the precipitate was exhaustively washed with methanol before drying *in vacuo* at room temperature. Successful polymerization to very high molecular weight polyacrylamide requires very small quantities of initiator and high purity of monomer and solvent.

The polymers are conveniently characterized by their reduced viscosities at 0.5% (w/v) concentration in water at 25°C. The intrinsic viscosity in water at 30°C was also found for two of the samples: the literature contains two Mark-Houwink equations for polyacrylamide,

$$[\eta] = 6.31 \times 10^{-5} \, [\bar{M}_v]^{0.80} \qquad (1)$$

given by Scholtan,[8] and

$$[\eta] = 6.8 \times 10^{-4} \, [\bar{M}_v]^{0.66} \qquad (2)$$

by Dainton et al.[9] Unfortunately, both samples lie outside the molecular weight range for which eqs. (1) and (2) were validated and, in any event, the agreement between these equations is poor. The extrapolated values are included in Table I; the data are also used to estimate the radius of gyration of the polyacrylamides in solution by application of the Flory-Fox[10] equation. Again, there is considerable discrepancy between the values deduced on the basis of eqs. (1) and (2), and the mean values recorded must be regarded as rough estimates only.

The sample preparation and testing used in the present study follow procedures standard to the industry. However, since these methods are not well known outside their specialized field and because the understanding of experimental observations requires familiarity with practical procedures, a relatively full description is given in the following sections.

Pulp Stock

The cellulose fibers used throughout this experimental work were derived from a single bale of Kaukaus bleached sulfate pulp. This was disintegrated and beaten following standard practice.[11] Pulp, 360 ± 5 g, was wetted with distilled water, torn into small pieces, and placed in a Weverk disintegrator with 10 liters of distilled water. A period of 10 min of disintegration with the shaft rotating at ca. 1750 rpm was sufficient to separate the fibers. This batch was then beaten

TABLE I
Polymer Characterization Data

Code	[Initiator]/ [Monomer][a]	η_{sp}/c[b]	$\bar{M}_v \times 10^{-5}$[c]	$\bar{M}_v \times 10^{-5}$[d]	$\langle s^2 \rangle^{1/2}$[e]	Specific conductivity $\times 10^5$[f]	% Hydrolysis
PAM-1	1.0×10^{-4}	0.74	(0.56)	(0.13)	67	2.65	0.1
PAM-2	5.0×10^{-5}	1.24	(3.67)	(1.29)	197	—	0.1
PAM-3	6.0×10^{-6}	5.83	9.25	4.08	396	0.72	—
PAM-4	5.0×10^{-7}	29.9	24.5	13.4	733	—	—
PAM-5	4.0×10^{-7}	52.0	(34.3)	(20.0)	905	0.54	—
PAM-6	3.0×10^{-7}	105.8	(53.0)	(34.2)	1190	—	—
PAM-7	2.5×10^{-7}	236.5	(87.3)	(63.0)	1640	0.75	—

[a] Molar ratio of equimolar persulfate and bisulfate to acrylamide.
[b] dl/g at 0.5% (w/v) in water at 25°C.
[c] Equation (1).
[d] Equation (2).
[e] Radius of gyration (Å).
[f] 0.1% (w/v) in water at 25°C (ohm^{-1}·cm^{-1}).

at 23°C in a Weverk Valley beater. In this, the pulp stock is recirculated through a region of high shear between a roller (rotating at 500 ± 10 rpm) and a bed-plate so mounted that pressure could be exerted vertically against the roller by a system of levers. The operation is as follows: without weight on the bed-plate lever, circulation of 10 liters of distilled water was started by switching on the roller motor. The disintegrated stock was then added together with sufficient water to bring the total volume in the beater to 23 liters, corresponding to a stock consistency of 1.57% (w/v). After 5 min of circulation, beating was commenced by weighting the bed-plate lever so as to exert a force equivalent to 10.7 ± 0.1 kg. The beating was continued for approximately 1 hr until the measured wetness reached the value adopted as standard (45° S.R.). The Schopper-Riegler value is a measure of the rate at which water drains from a stock suspension through a standard wire mesh[12] and is a parameter widely used in papermaking as a measure of the extent of fiber breakdown during the beating process.

The Schopper-Riegler tester has a container with a wire mesh as its base which may be closed by a bell valve. This valve is opened after filling with the stock. The draining water is split between two nozzles, one vertically below the wire, the other mounted at the side of the collecting vessel; the relative volumes collected via the two orifices is a measure of the ease of the drainage through the forming pad of fibers. The water from the side nozzle is collected in a glass receiver graduated (zero to 90) in °S.R. A sample of stock is taken from the beater of sufficient volume to contain about 2 g of fibers on a dry weight basis. This is diluted to 1 liter at approximately 20°C and then poured from one measuring cylinder to another to obtain uniform fiber distribution. Five sec after pouring into the wetness tester, the bell valve is released and the apparent °S.R. determined. The weight of fibers is found by drying the pad collected on the mesh; when this is different from 2 g, a correction is made to the initially determined wetness value from calibration curves supplied with the instrument.

The beaten stock was stored in a polythene container with a trace of sodium pentachlorophenate as preservative. The consistency of a paper stock is the weight of fibers on a dry basis to 100 ml of stock and was determined after beating to 45°S.R. by the standard method.[13]

Sheet Preparation

Again, a standard method[14] was followed. Beaten stock of measured consistency was diluted to 1.2%, and 2 liters were placed in a bench disintegrator to which was added 2.4 g titanium dioxide (Tioxide A-HR, Tioxide International Ltd.). This is a steam-micronized anatase made by the sulfate process which is uncoated and is 98–99% TiO_2. The particle diameter of this self-dispersing pigment is approximately 140 nm.

The titanium dioxide was mixed with the stock by stirring for 25 min in the bench disintegrator with the propellor shaft rotating at 3000 rpm, diluted to 8 liters, and then used immediately for sheet formation; this quantity is sufficient for ten sheets of paper. The British Standard Sheet Machine of 7-liter capacity was used; this is fitted with a 150-mesh wire on which the sheet is formed, together with a perforated disk agitator. With both the water and drainage cocks of the machine closed, the cavity below the wire was filled with water, taking care to avoid trapped air bubbles. With the cylinder of the sheet machine in the

vertical, closed position, 6 liters of distilled water, previously brought to the required pH by sodium hydroxide or hydrochloric acid, were added. This was followed by the stock containing pigment, fibers, and dissolved polymer. The polymer solution was diluted to 400 ml and was smoothly poured into a beaker containing an equal volume of the stock taken from the bench disintegrator. The liquid was poured back and forth between two beakers three times and then into the sheet machine. More water (at the required pH) was immediately added up to the graduation (7 liter) mark of the machine.

The stock was mixed by moving the perforated disk up and down five times within about 4 sec, and it was then slowly removed. Five sec after mixing, the drainage cock was opened to form the sheet. During this interval, the pH of the stock was rapidly checked. The water temperature had been checked to be 20 ± 0.5°C prior to pouring into the machine. A stopwatch was started when drainage commenced and was stopped when the liquid surface disappeared through the formed sheet. Quoted drainage times are the mean of duplicate determinations and reproduce within 5%; unlike the standard method,[15] they are not corrected to a standard sheet basis weight although the conditions employed are such as to be close to the standard method.

Immediately the water had drained from the sheet, the cylinder was tilted to expose the wet sheet on the wire. Removal of the sheet, "couching," was as described below. Duplicate sheets were prepared at each level of polymer addition.

Couching the sheet off the wire was achieved by placing two pieces of standard blotting paper over the wet sheet with the smooth side down. The flat brass couch plate was laid centrally on the blotters and the couch roll gently placed in the middle of the plate. The roll was moved back and forth to within 5 mm of the plate edge without placing extra pressure on the roll; this was done four times. The formed sheet now adheres to the underside of the couch blotter when the assembly is removed from the wire. The couch blotter and the sheet were placed in a press and a polished plate (158 mm diameter, 0.5 mm thick) placed on top; this is then covered with a dry piece of blotting paper ready to receive the next couch blotter and sheet. A stack of seven sheets is made vertical with a template and then pressed at 50 lb/in.^{2} for 5 min. On removal, the sheets now adhere to the plates. These are now restacked, test sheet uppermost, with the smooth side of a fresh blotter in contact with the paper and pressed a second time at 50 lb/in.^{2} for 2 min.

Finally, the test sheets on their plates are placed in drying rings. These brass rings fit into each other to clamp each plate and sheet around the periphery, and the stack is dried at 50% relative humidity at 23°.

Determination of Retention and Sheet Properties

Sheets, previously tested for porosity and opacity (q.v), were oven dried at 105°C to constant weight. Sheet weights in duplicate runs agreed to within 1%, and the overall average of all preparations was 1.2 g (±3%). After weighing, the folded sheet was placed in a covered platinum crucible and ashed at 925°C for 5 min.[16] The weight of titanium dioxide is the weight of ash less than that found from filler-free sheets (3.5 mg per sheet). The retention is quoted as the percentage of the initially added titanium dioxide (120 mg). Retention figures were reproducible within a range of 3% of the mean.

Air porosities of the paper conditioned at 50% relative humidity and 23°C were measured with a Bendsten tester by determining the air flow rate through a test area of 10 cm^2 under a pressure head equivalent to 15 cm water. Measurements were made over five different positions of the sheet (wire side down), and the mean (±5%) of the ten values from duplicate sheets was reported.

The contrast ratio method of determining the opacity of conditioned sheets is based on finding the diffuse reflectance R_B when the paper is backed with a black surface (≯0.005 reflectance) and the diffuse reflectance R_W of the same surface backed with a white surface of absolute reflectance of 0.89.[17] The contrast ratio is defined as 100 (R_B/R_W). Five measurements were made over sections of each sheet, and the mean of the ten values obtained from the duplicate sheets is reported; the mean values for each sheet agree with each other to within 0.5%.

Surface Areas

Fibers. A sample of beaten stock was diluted with twice its volume of acetone and the fibers allowed to settle. The clear layer was decanted off and replaced by acetone; after settling, the supernatant was replaced by a further addition of acetone which was left for 24 hr. Benzene was then added to the fibers from which the acetone had been filtered off; benzene was added during the filtration to prevent exposure to the atmosphere and drying of the fiber mat. When the acetone had been fully replaced by benzene, the wet fibers were allowed to soak in benzene for several days before being freeze dried. The dried, well-separated fibers were measured directly for their surface area without being exposed to moist atmosphere. After degassing at 105°C for 2 hr, the adsorption isotherm of nitrogen at 77°K was measured in a volumetric apparatus similar to that described in British Standard 4359.[18] Application of the BET equation, assuming a molecular area for nitrogen of 16.2 Å^2, gave a surface area of 25.5 m^2/g.

Pigment. This was degassed at 150°C prior to the BET determination, which yielded a specific surface area of 9.0 m^2/g.

Flocculation Measurements

Fiber Flocculation. A sample of the beaten stock was diluted to 0.2% consistency and any necessary pH adjustments made. Of this sample, 400 ml was measured into one of a set of identical 500-ml graduated cylinders so that it contained 0.80 ± 0.016 g fibers. The required quantity of polymer solution in water was diluted to 100 ml and added to the cylinder. The contents of each stoppered cylinder were immediately mixed by smoothly inverting the cylinder ten times. These flocculation measurements were performed in quadruplicate at 20 ± 1°C, three types of characterization being made. The subsidence time was noted for the boundary between the subsiding fiber mass and the relatively clear supernatant to fall down to the 250-ml graduation mark, timing being started immediately after mixing. Sediment volumes were read (to the nearest 2 ml) after 15 hr, and the equilibrium pH was also determined at this time. After noting the sediment volume, 10-ml samples were removed by pipet lowered to the 250-ml graduation mark. The turbidity of the suspended fiber was measured at 441 nm wavelength at a 40 mm path length with distilled water as a reference

using a Unicam SP600 spectrophotometer. Subsidence times were reproducible to within 5%, and sediment volumes and supernatant optical density to within 3%.

Pigment Flocculation. A suspension of 0.24 g titanium dioxide in 4.8 liters distilled water was made by stirring. After adjusting the pH as required, 400 ml was poured into graduated cylinders as above and 100-ml polymer solution added. After mixing as before, the optical density at the 250-ml level was found after 15 hr of settling time. Recorded values are for 10-mm path length at 441 nm; the quadruplicate runs, made at 20°C, agreed within 1%.

Coflocculation. A sample of beaten stock was diluted to 0.05% consistency and 0.24 g titanium dioxide dispersed in it by stirring. The fiber/pigment ratio is thus the same as used in making the hand-sheets.

Again, 400 ml was added to a 500-ml graduated cylinder, 100 ml polymer solution of the required concentration added, and the contents mixed by ten inversions. After settling for 20 min, a sample was removed from the 250-ml level and the optical density (10 mm, 441 nm) found; suspended pigment particles contribute predominantly to this turbidity. The reproducibility was within 2% for measurements made in quadruplicate at 20°C.

Polymer Adsorption

Equilibrium polymer adsorption was calculated from the difference between the concentrations of the initial solution and the supernatant after 15 hr of contact. Preliminary measurements showed that the adsorption of PAM 7 on titanium dioxide was constant between contact times of 7 hr and 15 hr; on fibers, the adsorption is practically constant over the same time range. After the adsorption period, the suspensions were centrifuged in two stages in stoppered tubes. A first-stage separation was made at 3000 rpm for 5 min and the supernatant decanted into a second tube and then centrifuged at 5000 rpm for 1.0 to 1.5 hr. This extensive centrifugation was necessary to clear the fine pigment particles and fibers from the supernatant. A sample was tested for optical density (40 mm, 441 nm) against distilled water as reference; only when the value was less than 0.005 was the supernatant analyzed for polymer concentration.

Polyacrylamides in water exhibit a strong absorption in the far UV peaking at 191.5 nm, and this was used to estimate solution concentration. As the Beer's law plot was accurately linear only up to approximately 10 mg/l., careful dilution

TABLE II
Concentrations and Polymer/Solid Ratios in Experimental Procedures

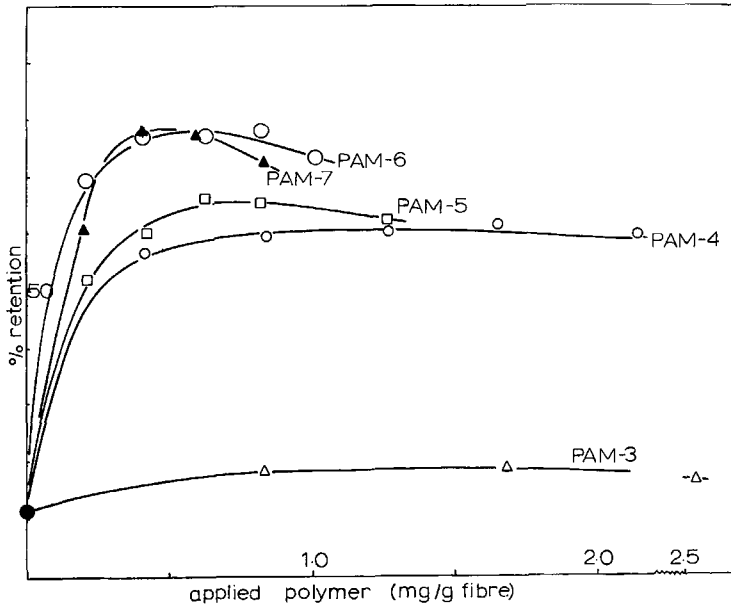| Method | Concentration, mg/l. | | Polymer/solid ratio $\times 10^3$ | |
	Fiber	Pigment	Polymer (range)	Polymer/ fiber	Polymer/ pigment
Sheet formation	170	17	0.02–0.40	0.1–2.0	1.0–20
Fiber flocculation	1600	—	0.16–8.0	0.1–5.0	—
Pigment flocculation	—	40	0.10–20	—	2.5–500
Coflocculation	400	40	0.20–12	0.5–30	5–300
Adsorption (fiber)	10, –20,000	—	30–100	1.0–10	—
Adsorption (pigment)	—	ca. 20,000	10–100	—	0.5–5

Fig. 1. Retention of titanium dioxide in hand-made sheets as function of amount of added poly-acrylamide at pH 6.5.

was necessary to bring supernatants to suitable concentration for spectrophotometry.   Reproducibility is poor (within 20%) on fibers, where the adsorption is low, but is around 4% on titanium dioxide.

Comparison of Methods

Practical considerations enforce differing concentrations, both of solids and polymers, in the various methods.   Table II gives both the absolute "concentrations" and the polymer/solid ratios for the various investigational techniques. The ranges of the latter variable exhibit considerable overlap from method to method.

RESULTS

Pigment Retention

Figure 1 shows the % retention at pH 6.5 of titanium dioxide in standard paper sheets, prepared as described above, as a function of the amount of added poly-

TABLE III
pH Dependence of Retention Efficiency

Polymer code	Applied polymer	Retention of titanium dioxide, %		
		pH 4.5	pH 6.5	pH 8.0
—	zero	19.8	11.9	10.8
PAM-6	0.61	79.1	77.5	76.9
	0.82	80.0	78.4	78.0
PAM-7	0.61	77.3	77.7	76.0
	0.82	75.5	72.5	74.7

acrylamide for five polymers of various molecular weights. Little retention is shown until the polyacrylamide is of high molecular weight (greater than approximately 5×10^5). The retention curves show a flat maximum which sharpens as the molecular weight, and retention, increases; thus, PAM-7 has an optimum retention efficiency which is not significantly greater than PAM-6, but has a notably sharper maximum. The pH dependence is small and is given in Table III. Measurements made with a commercial, nonionic acrylamide polymer show little variation in reduced viscosity and, hence, of coil size over the pH range covered in these retention measurements.

Flocculation Studies

Fiber flocculation was studied by the methods described above, and the results are summarized in Table IV. Consideration of these data suggests that the packing of the eventual sediment is not affected by the presence of polyacrylamide. The optical densities indicate that fiber fines have a long-term stability; polyacrylamide reduces the amount of such suspended fibers only slightly, although there is an indication of a maximum effect at a polymer loading of approximately 1 mg/g fiber.

Judged by the rate of subsidence, PAM-5 is not a flocculant for the fibers and must be presumed to have too small a coil size for a bridging mechanism to be

TABLE IV
Fiber Flocculation by Polyacrylamides (pH 6.4)

Applied polymer, mg/g fiber	Subsidence time, min		Optical density		Sediment volume, ml	
	PAM-5	PAM-7	PAM-5	PAM-7	PAM-5	PAM-7
0.0	22.0	22.0	0.292	0.292	112	112
1.25	21.3	18.0	0.268	0.232	115	114
2.50	22.2	14.1	0.272	0.246	116	115
3.75	20.6	15.5	0.272	0.251	115	111
5.00	21.4	17.1	0.276	0.262	115	111

TABLE V
Flocculation of Titanium Dioxide by High Molecular Weight Polyacrylamide

Applied polymer concentration, mg/l.	Optical density		
	pH 4.3	pH 6.0	pH 8.5
0.0	0.11	0.57	0.58
0.2	0.15	0.55	0.58
0.4	0.23	0.55	0.58
0.6	0.26	0.57	0.61
0.8	0.21	0.58	0.61
1.0	0.18	0.58	0.59
1.6	0.25	—	—
2.0	0.25	0.54	0.53
4.0	0.28	0.54	0.54
10.0	0.32	0.56	0.58
20.0	0.34	0.58	0.58

operative; PAM-7 does speed up the rate of subsidence with a maximum effect around a loading of 3 mg/g fiber.

Pigment flocculation was studied with a high molecular weight commercial polyacrylamide generally similar to PAM-6 in retention behavior; the residual turbidity as found by the method described above is given at three pH values in Table V.

Significantly, all the data of Table V point to stabilization of the pigment dispersion and not to flocculation. First, in the absence of added polyacrylamide, stabilized suspensions are formed in neutral and alkaline solution; at these pH's, the high molecular weight polyacrylamide has no effect on colloid stability. At pH 4.3, however, the polymer stabilizes the dispersions of titanium dioxide; further measurements were made at this pH with lower molecular weight polymers (Table VI). Steric stabilization of dispersed solids by adsorbed macromolecules is characteristically associated with lower molecular weight polymers; PAM-2 and PAM-3 are good in this respect, and the poor performance of PAM-1 may be attributed to its low level of adsorption (see later).

In studies of coflocculation of mixed dispersions having a fiber:pigment ratio the same as in sheet formation, the turbidity was judged after a relatively short settling time (20 min). The general behavior is exemplified in Figure 2, where the commercial polyacrylamide was employed. Small additions of polymer have a marked flocculation effect, but overdosing partially restabilizes the system. It is the particles of titanium dioxide which contribute most of the measured turbidity as (see Table IV) unsettled fibers would contribute, at a maximum, an optical density of less than 0.02. The pH dependence is less severe than with pigment alone (Table V). To judge the effect of polyacrylamide molecular weight, the optimum conditions, corresponding to the minima of Figure 2, are reported. To be consistent with the retention data, the polymer loading is given in terms of added polymer per gram fiber (Table VII). The data of Table VII show that the lower molecular weight polymers, as in retention, have little effect, whereas the higher molecular weights are of similar, high efficiency.

Polymer Adsorption

Equilibrium adsorption isotherms for several of the polyacrylamides at pH 6.5 are shown for fibers and pigment in Figures 3 and 4, respectively. The extent

TABLE VI
Effect of Polyacrylamides on Dispersions of Titanium Dioxide at pH 4.3

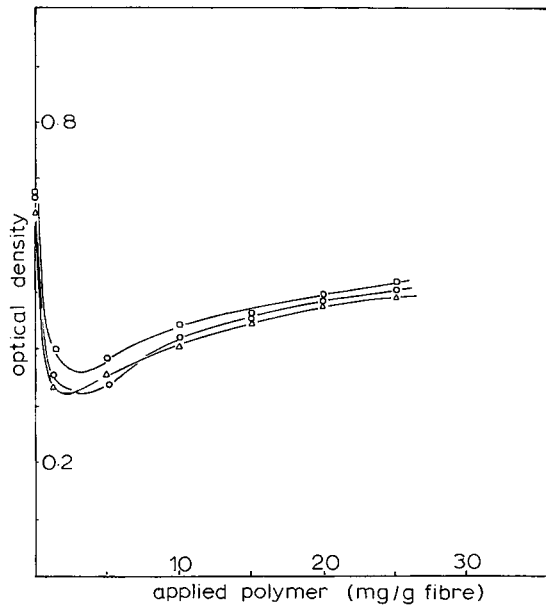| Applied polymer concentration, mg/l.	Optical density		
	PAM-1	PAM-2	PAM-3
1.0	0.12	0.52	0.34
2.0	0.08	0.56	0.57
3.0	0.11	0.53	0.50
4.0	0.09	0.55	0.57
6.0	0.10	0.28	0.57
7.0	0.08	0.54	0.57
8.0	0.11	0.46	0.54
10.0	0.08	0.39	0.57
11.0	0.09	0.48	0.58

Fig. 2. Coflocculation of pigment and fibers by high molecular weight polyacrylamide at various pH's. Optical density at midheight after 20 min settling as function of amount of added polymer: (△) pH 4.3; (○) pH 6.2; (□) pH 7.8.

of adsorption on fibers is low, but is clearly dependent on molecular weight; plateau adsorptions are exhibited at low solution concentrations which are, however, in excess of those employed in sheet formation and in coflocculation studies. Adsorptions are higher on titanium dioxide, with a molecular weight dependence which becomes less evident at high molecular weights. The pH dependence of adsorption was not examined for these polyacrylamides, but the commercial polymer showed a slight decrease in adsorption, on both fibers and pigments, as the pH is raised from 4.3 to 8.2.

TABLE VII
Effect of Polyacrylamides on Coflocculation Behavior

	pH 4.5		pH 6.4		pH 8.4	
Polymer code	Optimum applied polymer, mg/g fiber	Minimum optical density	Optimum applied polymer, mg/g fiber	Minimum optical density	Optimum applied polymer, mg/g fiber	Minimum optical density
PAM-2	n.d.[a]	0.62	n.d.[a]	0.62	n.d.[a]	0.62
PAM-3	19 ± 1	0.59	20 ± 1	0.59	20 ± 1	0.60
PAM-4	10 ± 1	0.42	11.5 ± 0.1	0.47	12 ± 1	0.48
PAM-5	2.0 ± 0.4	0.37	3.0 ± 0.4	0.37	3.0 ± 0.4	0.38
PAM-6	1.10 ± 0.25	0.29	1.80 ± 0.25	0.31	1.95 ± 0.05	0.32
PAM-7	1.25 ± 0.25	0.29	1.30 ± 0.25	0.29	1.50 ± 0.05	0.30

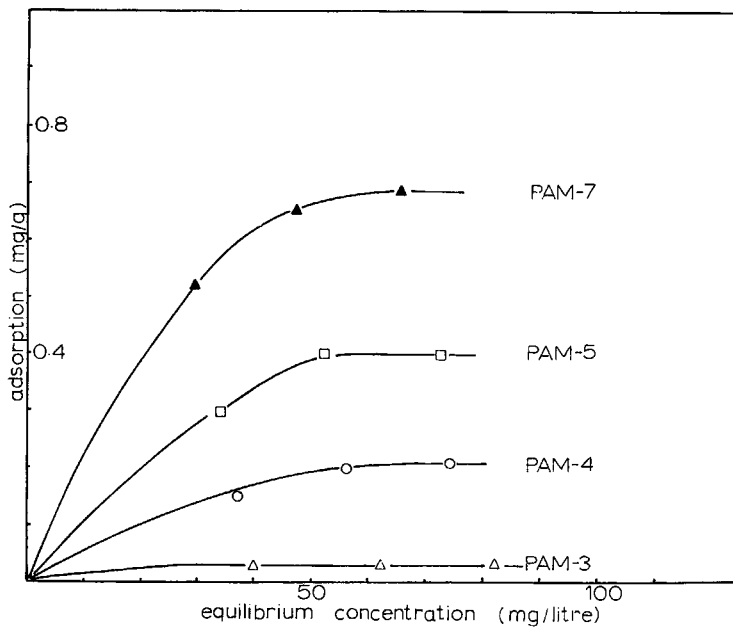[a] No restabilization at higher polymer loadings.

Fig. 3. Adsorption isotherms of polyacrylamides on fibers at pH 6.5.
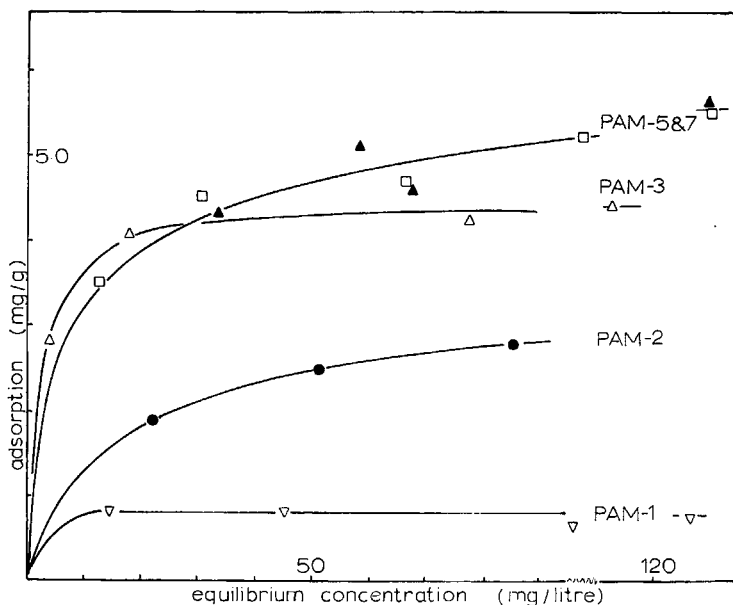

Fig. 4. Adsorption isotherms of polyacrylamides on pigment at pH 6.5.

Drainage Times and Sheet Properties

The drainage time in sheet formation is shown in Figure 5 as a function of the polyacrylamide content relative to fiber.   There is a marked correspondence to the retention results (Fig. 1) in that PAM-3 has an insignificant effect on either retention or drainage; the greater the retention efficiency of the polyacrylamide,
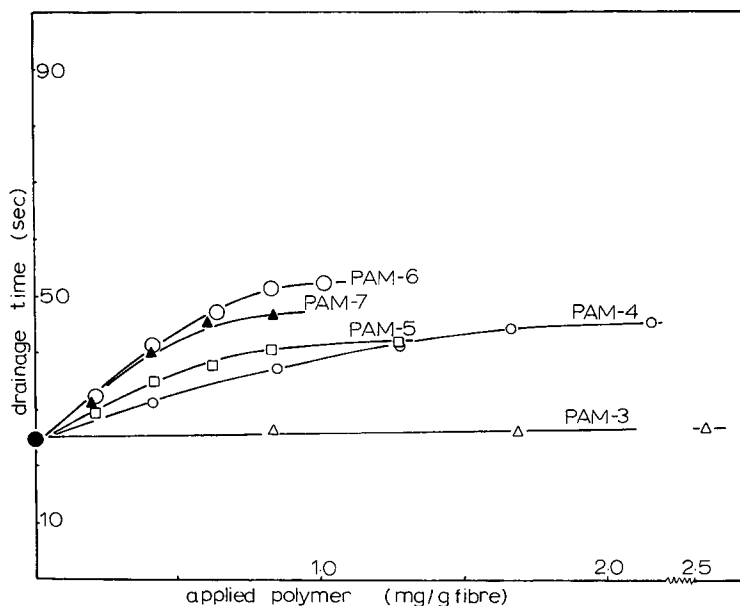
Fig. 5. Drainage time in sheet formation at pH 6.5 as function amount of added polyacrylamide.

the slower the drainage through the forming sheet. However, whereas retention of titanium dioxide drops off at higher polymer doses, this is not reflected in the drainage times. The drainage rate is generally taken to be related to an effective surface area of the forming sheet; if this is so, then the specific surface of the pad is higher even though less titanium dioxide is retained at the higher polymer loadings.

The pH dependence of the drainage rate is small (Table VIII). The air porosity of dried sheets is 12.7 ± 10% ml/min, and no dependence on polymer loading or molecular weight was evident. The sheet opacities are directly related to the retention of titanium dioxide. In Figure 6, the intercept represents the opacity of a filler-free sheet. Again the pH dependence is small (Table IX).

DISCUSSION

In this model papermaking system, most of the titanium dioxide passes through the fiber pad unless high molecular weight polymer is present. Inspection of Table III shows that rather greater pigment retention, in the absence

TABLE VIII
pH Dependence of Drainage Time in Sheet Formation

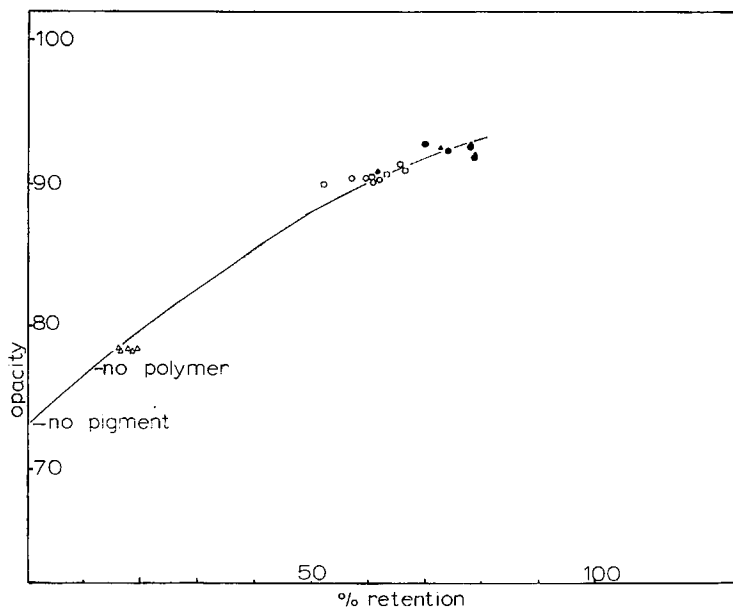| Polymer code	Applied polymer, mg/g fiber	Drainage time, sec		
		pH 4.5	pH 6.5	pH 8.0
—	zero	23.4	24.8	25.1
PAM-6	0.61	43.7	47.2	48.4
	0.82	48.3	51.5	51.9
PAM-7	0.61	42.9	45.2	43.9
	0.82	46.2	46.9	48.4

Fig. 6. Opacity (% contrast ratio) of dry sheet as function of retention of titanium dioxide in presence of polyacrylamides: (△) PAM-3; (○) PAM-4; (□) PAM-5; (●) PAM-6; (▲) PAM-7.

of polyacrylamide, is obtained under acid conditions, but the effect is small and is barely reflected in the rate of sheet formation (Table VIII) and in sheet opacity (Table IX). It is noticeable that the greatest effect of pH on retention is exhibited as the isoelectric point of the titanium dioxide is approached. According to Schindler and Gamsjäger,[19] the point of zero charge is at pH 6.4. However, addition of polymer overcomes any pH dependence of retention.

The general shapes of the curves of Figure 1 are closely analogous to those for the flocculation of solid dispersions by added polymers. In the flocculation of kaolin suspensions by polyacrylamides, as reported by Wilde and Dexter,[20] lower molecular weight polymer has no effect; an overdosing effect is exhibited which becomes increasingly severe as the molecular weight reaches very high values. Sakaguchi and Nagase,[21] also working with kaolin and polyacrylamides, found similar behavior. Flocculation effects of this kind require, of course, that the polymer (flocculant or retention aid) be adsorbed on the particles. The equilibrium adsorption isotherms of Figures 3 and 4, although at absolute polymer concentrations well in excess of those employed in sheet formation, but with

TABLE IX
pH Dependence of Sheet Opacity

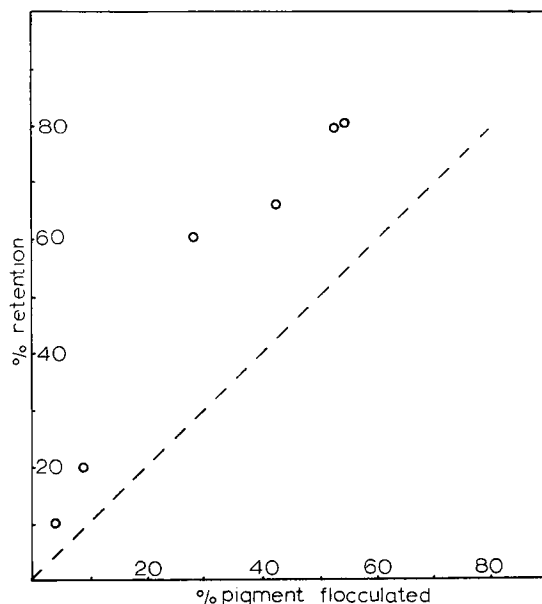| Polymer code	Applied polymer, mg/g fiber	Opacity (contrast ratio %)		
		pH 4.5	pH 6.5	pH 8.0
—	zero	77.9	76.3	75.9
PAM-6	0.61	92.9	92.4	92.7
	0.82	92.5	91.9	92.9
PAM-7	0.61	92.3	92.7	92.1
	0.82	92.2	92.5	92.2

Fig. 7. Retention of titanium dioxide in hand-made sheets vs. retained polymer in coflocculation test.

similar polymer/particle ratios, are valuable in indicating the propensity of the polyacrylamides to be adsorbed. Thus, a greater amount of polymer is adsorbed at higher molecular weights, and, on a mass basis, the titanium dioxide takes up approximately ten times as much polymer as the cellulose fibers.

In sheet formation, there is a tenfold excess of fiber, but the pigment particles are more numerous. Further, the elapsed time between addition of polymer to the stock and completion of sheet formation is only about 1 min; the configuration and amount of adsorbed polymer may be very different from the equilibrium state. In these short times, the adsorption will be controlled by collisions between the macromolecules and the solid particles; in this process, the greater number of pigment particles will be counterbalanced to some extent by the high axial ratio of the fibers, each sweeping out a relatively large solution volume. There would seem, therefore, to be ample opportunity for a heteroflocculation between pigment and fiber.

The retention behavior can be conceived as a consequence of several alternative processes. First, the retention aid may produce fiber–fiber flocculation and so lead to a sheet better able to filter the pigment particles. Secondly, a bridging of pigment particles would lead to agglomerates which are now large enough to be held within the fiber pad. Or, finally, the polymer may bond fiber to pigment by heteroflocculation ensuring a high pigment retention in the sheet.

The effect of adding polyacrylamides to separate dispersions of the solid particles is informative. Table IV shows clearly that a limited bridging flocculation between fibers is exhibited only by the sample of very high molecular weight. However, PAM-5, which is quite good in retention, has hardly any effect on aqueous dispersions of fiber alone. When pigment dispersions are considered, it is seen that, rather than flocculation, the colloid stability is enhanced, especially with polyacrylamides of moderate molecular weight and at low pH. The be-

havior of the separate dispersions is very different to that of mixed dispersions, as shown in Figure 2. The general concordance between the coflocculation results and retention performance is further evidence of a heteroflocculation mechanism. The optimum polymer loading in the coflocculation experiments (Table VII) is certainly higher than in sheet formation; however, the dilution and time scales are different in the two phenomena. The residual supernatant turbidity (see Table VII) in coflocculation must be largely derived from suspended, relatively stable particles of titanium dioxide. Whether these are coagglomerated with fiber fines is not known.

Assuming all the measured turbidity to be due to titanium dioxide, an estimate may be made of the fraction of added pigment which has settled (within 20 min) during coflocculation, and this is compared to retention performance. Figure 7 makes this comparison for the optimum conditions in both types of experiments. Some of the short-fall may be attributable to the assumptions made in calculating the "retained" titanium dioxide in coflocculation, but it seems that part of the discrepancy is a measure of an enhanced trapping of pigment by the sheet formed by heterocoagulated particles during the papermaking process. The increased drainage time may be an indication of this filtration contribution to retention.

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