

## Water-Soluble Polymers as Retention Aids in a Model Papermaking System. II. Poly(vinylpyridines)

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### Synopsis

Three poly(4-vinylpyridines) and a poly(2-vinylpyridine) were studied for their effectiveness at increasing the retention of titanium dioxide in a model papermaking system at pH 3.8. All the polymers are very efficient retention aids and do not greatly increase the time for the paper sheet to be formed. They are well adsorbed by both cellulose fibers and titanium dioxide. Although fiber suspensions are weakly flocculated by the poly(vinylpyridines), pigment suspensions are stabilized. Flocculation studies on mixed suspensions show that the poly(vinylpyridines) have a powerful heterocoagulation effect which mirrors the retention results. Some results are also reported in which the pH is brought to 6.5; under these conditions, polymer adsorption and its consequent effects compete with polymer precipitation.

### INTRODUCTION

In the preceding paper,<sup>1</sup> we discussed the behavior of polyacrylamides in the retention of titanium dioxide during the formation of a paper sheet. The polyacrylamides may be presumed to adsorb to both cellulose fiber and titanium dioxide surfaces by virtue of hydrogen bonding. We now report a parallel study using the more polar poly(vinylpyridines) which are expected to show dipolar interaction with the solid surfaces employed here.

### EXPERIMENTAL

#### Polymer Synthesis and Characterization

4-Vinylpyridine (Koch Light) was percolated through a column of alumina to remove inhibitor; this treatment also decolorized the as-supplied monomer. One poly(vinylpyridine) (P4VP-1) was prepared by radical polymerization; the monomer was heated at 60°C for 6 hr in the presence of 1% benzoyl peroxide. The reaction product was taken up in methanol and reprecipitated by water; after washing, it was dried *in vacuo* at room temperature.

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The other poly(4-vinylpyridines) were made by polymerization in concentrated sulfuric acid by a method recently reported.<sup>2</sup> Monomer was added dropwise to 98% sulfuric acid in a flask at 0°C. The quantities used were such that the molar ratio of excess acid to the formed 4-vinylpyridinium bisulfate was 2.6. Sample P4VP-2 was prepared by allowing the reaction to proceed for one week at room temperature; P4VP-3 was derived from the reaction at 0°C for three weeks. In both cases, polymerization was terminated by the addition of a large excess of water and followed by neutralization of the acid with solid sodium carbonate. The precipitated polymer was thoroughly washed before drying *in vacuo*.

A sample of 2-vinylpyridine (Koch Light) was found to have partially polymerized on standing at laboratory temperature for about three years. The polymer (P2VP) was dissolved in methanol and then precipitated with water; further purification and drying was as before. All the poly(vinylpyridines) were obtained as off-white powders soluble in dilute acid. Intrinsic viscosities were measured at 25°C in the mixed solvent 92/8 ethanol/water and molecular weights calculated from published expressions (Table I).<sup>3,4</sup>

It was found that the sulfuric acid polymerization proceeded only if the monomer had been purified by alumina treatment. The infrared spectra of both radical- and ionic-polymerized polymers were identical; thus, samples P4VP-2 and P4VP-3 have repeat units linked solely by the vinyl substituent and not through the pyridine ring. The spectra of poly(4-vinylpyridine) and poly(2-vinylpyridine) differ mostly in the 1000–1600  $\text{cm}^{-1}$  region.

### Beating of Pulp Stock, Sheet Formation, Measurement of Pigment Retention, and Flocculation Studies

There were as in the preceding paper. Supernatant concentrations for adsorption studies were found from the turbidity of solutions which had been treated with base. A known volume was taken from the supernatant after centrifugation and made up to approximately 40 ml in a 50-ml volumetric flask; 2 ml of a 1.5% (w/v) sodium hydroxide solution was added by pipet, the contents shaken, and made up to volume. After aging for 3 hr, the optical density (40 mm, 441 nm) was measured and compared with calibration graphs prepared for each poly(vinylpyridine).

TABLE I  
Polymer Characterization Data

Code	$[\eta]^c$	$\bar{M}_v$
P4VP-1 <sup>a</sup>	2.06	630,000 <sup>d</sup>
P4VP-2 <sup>b</sup>	1.79	520,000 <sup>d</sup>
P4VP-3 <sup>b</sup>	2.22	700,000 <sup>d</sup>
P2VP	2.21	681,000 <sup>e</sup>

<sup>a</sup> Radical polymerization.

<sup>b</sup> Ionic polymerization.

<sup>c</sup> dl/g in 92/8 ethanol/water at 25°C.

<sup>d</sup> Equation given in ref. 3.

<sup>e</sup> Equation given in ref. 4.

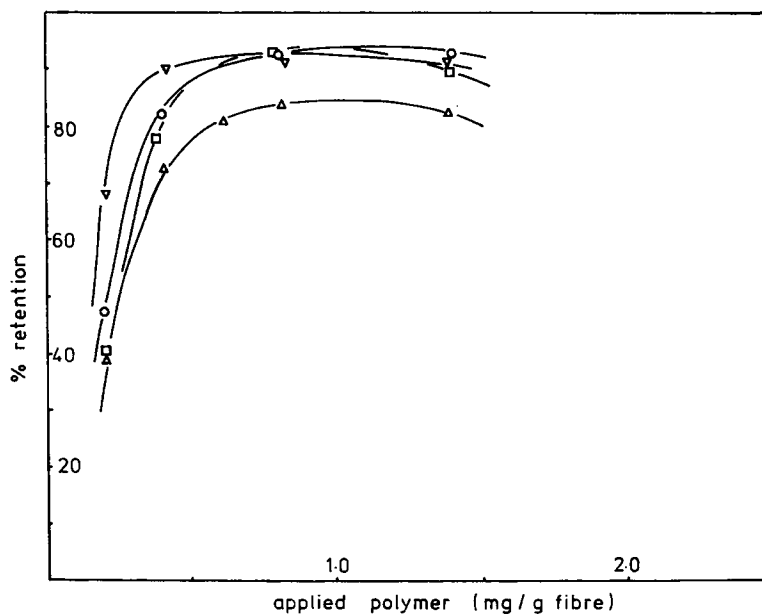


Fig. 1. Retention of titanium dioxide in hand-sheets as function of amount of added poly(vinylpyridines) at pH 3.8: ( $\Delta$ ) P4VP-1; ( $\circ$ ) P4VP-2; ( $\square$ ) P4VP-3; ( $\nabla$ ) P2VP.

## RESULTS

### Pigment Retention

Figure 1 shows the retention of titanium dioxide at pH 3.8 in the presence of various levels of the poly(vinylpyridine). At quite low loadings of poly(vinylpyridine), the retention values are increased from ca. 20% to over 80%. Two points should be noted, as they stand in contrast to the polyacrylamide studies.<sup>1</sup> First, the retention efficiency increases to a more shallow maximum than with the polyacrylamides. Second, the radically polymerized polymer (P4VP-1), although a good retention aid, is somewhat less efficient than the other samples.

Some measurements were also made by mixing the polymer solution at pH 3.8 with the fiber/pigment dispersion (1.2% in fibers) at the same pH. Immediately after the standard mixing procedure, the dispersion was poured into water

TABLE II  
Retention Efficiency at pH 6.5

Applied polymer, mg/g fiber	Retention, %			
	P4VP-1	P4VP-2	P4VP-3	P2VP
0	11.9	11.9	11.9	11.9
0.62	79.5	84.3	77.6	79.4
0.82	87.4 (24.1) <sup>a</sup>	86.2 (24.2) <sup>a</sup>	82.0 (25.6) <sup>a</sup>	84.0 (27.8) <sup>a</sup>
1.24	89.1	85.1	86.6	87.3

<sup>a</sup> Polymer solution added to stock at pH 6.5.

in the sheet machine which had been adjusted to give the papermaking stock a final pH of 6.5. The retentions (Table II) are similar to those in Figure 1, indicating that the effect of the poly(vinylpyridine) is complete within a few seconds and is not reversed by subsequent pH adjustment.

However, when the polymer solution was mixed with a fiber/pigment dispersion at pH 6.5 and then added to the sheet machine containing water at this pH, the retention values are very low (Table II). These observations suggest that immediately on bringing the poly(vinylpyridine) to neutral pH, it is precipitated before being able to act as a retention aid.

### Flocculation Studies

Fiber flocculation was studied as before; repeatabilities were within about 4–5% of the mean value quoted (Table III). At pH 3.8, small additions of all the poly(vinylpyridines) had a considerable effect on the fiber suspension. Although the rate of settling was noticeably slower, the polymers much reduced the quantity of suspended fiber fines in the supernatant and caused the formation of a more open sediment bed. Some parallel measurements were also made in which the fibers suspension was at a high pH such that, after addition of polymer solution, the final pH was  $6.5 \pm 0.1$ . In this case, precipitation of poly(vinylpyridine) is a competing process to its adsorption on fiber surfaces. Although a limited degree of clarification is observed, the addition of polymer has little effect on the subsidence rate or sediment volume.

TABLE III  
Fiber Flocculation by Poly(vinylpyridines) at pH 3.8 and pH 6.5

Applied polymer, mg/g fiber	Subsidence time, min		Optical density		Sediment volume, ml	
	pH 3.8	pH 6.5	pH 3.8	pH 6.5	pH 3.8	pH 6.5
			P4VP-1			
0	24.7	19.8	0.229	0.299	130	111
0.125	30.6	19.6	0.056	0.254	154	112
0.250	32.2	20.7	0.027	0.235	155	113
0.375	33.8	19.5	0.031	0.214	158	109
			P4VP-2			
0.125	31.0	21.8	0.035	0.299	149	112
0.250	32.8	24.7	0.026	0.178	158	117
0.375	34.2	24.6	0.035	0.113	155	115
			P4VP-3			
0.125	31.1	21.2	0.034	0.252	144	111
0.250	32.6	24.1	0.024	0.248	148	111
0.375	32.6	24.0	0.032	0.240	141	108
			P2VP			
0.125	30.1	19.4	0.083	0.285	145	108
0.250	32.2	21.8	0.026	0.251	153	116
0.375	32.5	19.5	0.032	0.234	157	118

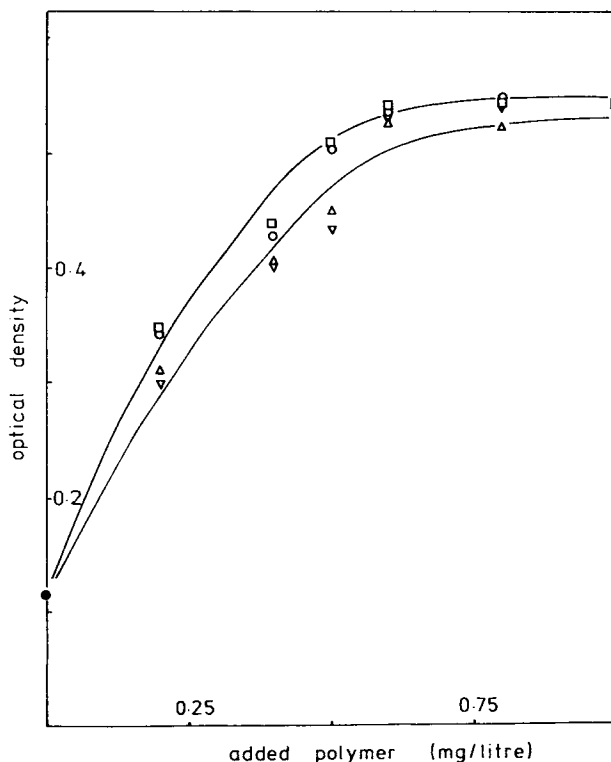


Fig. 2. Stabilization of dispersions of titanium dioxide at pH 3.8 by poly(vinylpyridines). Symbols as in Fig. 1.

The effect of the poly(vinylpyridines) on titanium dioxide suspensions was judged, as previously, by the supernatant turbidity after standing for 15 hr. Titanium dioxide in water at pH 3.8 coagulates and settles from the dispersion. Addition of polymers stabilizes the dispersion up to a plateau level (Fig. 2). At pH 6.5, dispersions of titanium dioxide are stable but are flocculated by the poly(vinylpyridines) (Fig. 3); this behavior suggests that adsorption, followed by bridging between particles, competes favorably with precipitation of the polymer.

Coflocculation studies were made as in the preceding paper.<sup>1</sup> As judged by the supernatant turbidity after 20 min of settling, all the poly(vinylpyridines) show strong coflocculation behavior, even at pH 6.8, where polymer precipitation is a competing process (Figs. 4 and 5). It is noticeable that the lowest molecular weight sample is the most efficient flocculant and that the 4-vinylpyridine polymers seem to be superior to the solitary poly(2-vinylpyridine). Typical polymer flocculation behavior, with noticeable restabilization of the suspension at higher polymer doses, is exhibited.

### Polymer Adsorption

The adsorption of P4VP-3 on pigment and on fibers at pH 3.8 was constant within the time period of 4–15 hr. Only equilibrium adsorption measurements,

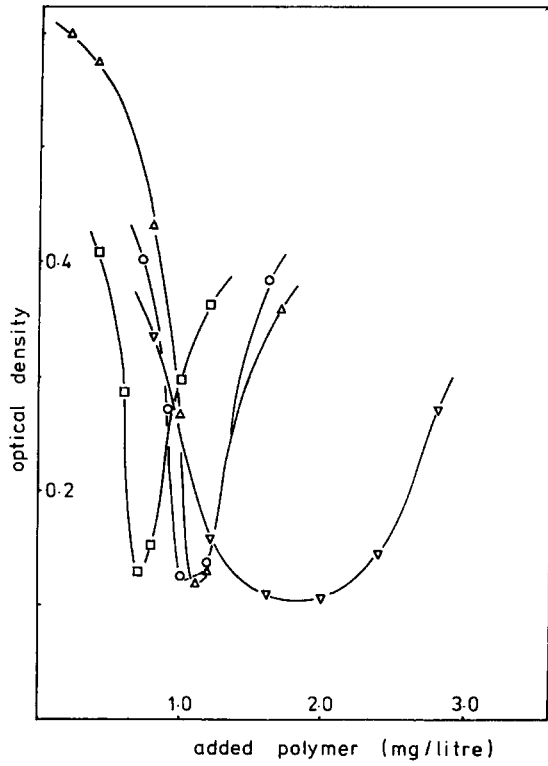


Fig. 3. Flocculation of dispersions of titanium dioxide at pH 6.5 by poly(vinylpyridines). Symbols as in Fig. 1.

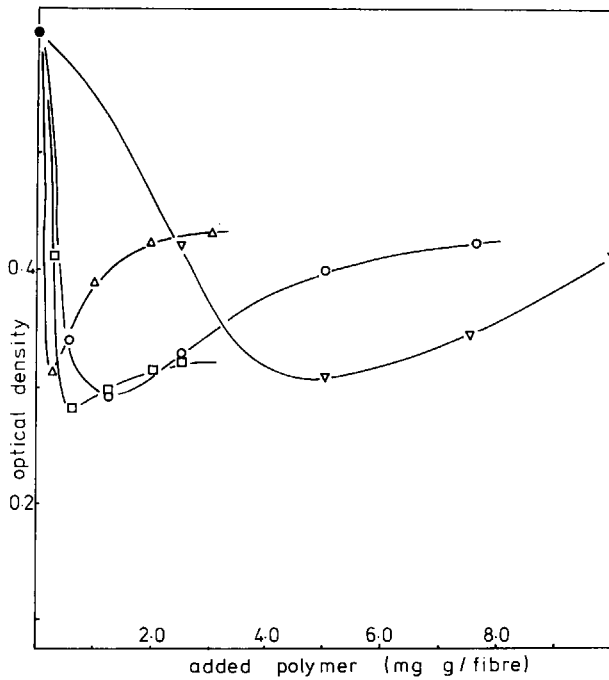


Fig. 4. Coflocculation of pigment and fibers at pH 3.8 by poly(vinylpyridines). Symbols as in Fig. 1.

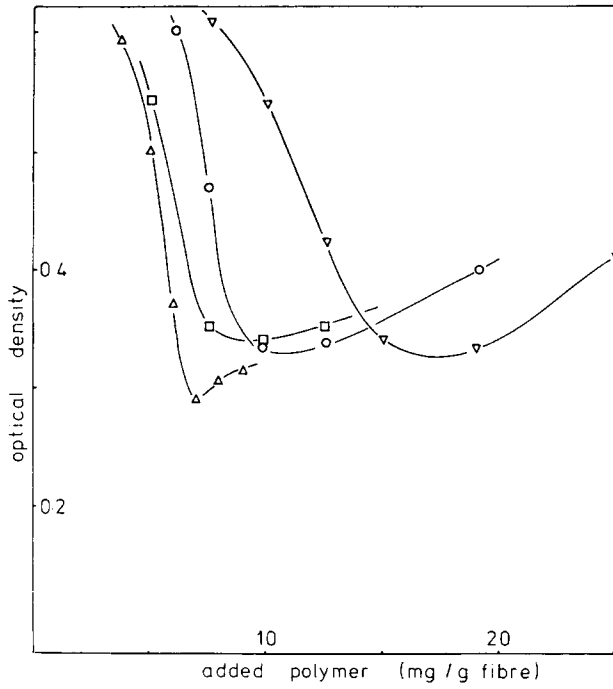


Fig. 5. Coflocculation of pigment and fibers at pH 6.5 by poly(vinylpyridines). Symbols as in Fig. 1.

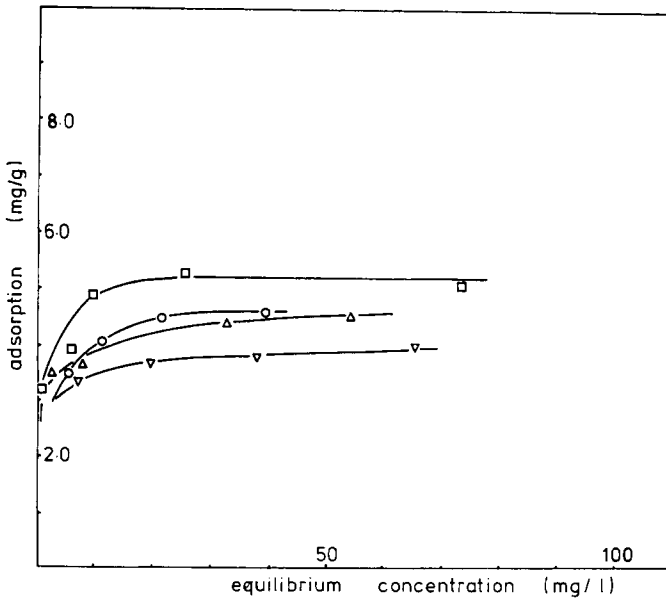


Fig. 6. Adsorption isotherms of poly(vinylpyridines) on fibers at pH 3.8. Symbols as in Fig. 1.

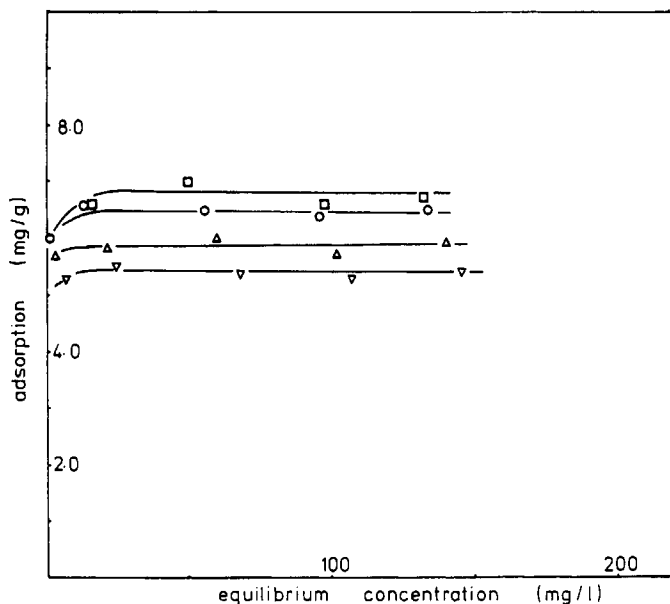


Fig. 7. Adsorption isotherms of poly(vinylpyridines) on pigment at pH 3.8. Symbols as in Fig. 1.

normally after 15 hr of contact with the adsorbent, were attempted; reproducibilities were around 3.5% and are considered acceptable at the low levels of adsorption recorded. The adsorption isotherms at pH 3.8 (Figs. 6 and 7) show that, at both surfaces, the intrinsic adsorbability of the poly(4-vinylpyridines) is slightly greater than that of the poly(2-vinylpyridine).

### Drainage Times and Sheet Properties

Addition of poly(vinylpyridines) increases the drainage time on sheet formation, although to a much lesser extent than the polyacrylamides<sup>1</sup> (Table IV).

A single relationship between sheet opacity and retention of titanium dioxide is found (Table V); the single line representing data at two pH values and all polymer loadings is drawn (without the data points as these overlap or superpose) in Figure 8, and a small but distinct improvement over the polyacrylamide curve is shown.

TABLE IV  
Drainage Time in Sheet Formation with Poly(vinylpyridines) at pH 3.8<sup>a</sup>

Applied polymer, mg/fiber	Drainage time, sec							
	pH 3.8				pH 6.5			
	P4VP-1	P4VP-2	P4VP-3	P2VP	P4VP-1	P4VP-2	P4VP-3	P2VP
0	23.4	23.4	23.4	23.4	24.8	24.8	24.8	24.8
0.21	31.0	29.5	27.0	29.0	—	—	—	—
0.41	33.3	33.1	30.6	29.7	—	—	—	—
0.62	36.5	—	—	—	30.8	32.2	29.1	30.2
0.82	37.0	32.3	29.8	28.2	32.5(26.0)	32.1(23.1)	30.3(24.6)	29.5(24.5)
1.25	—	—	—	—	33.4	32.4	31.4	28.8
1.39	37.2	32.6	29.3	28.5	—	—	—	—

<sup>a</sup> Values in parentheses: stock and polymer mixed at pH 6.5 before adding to sheet machine.



## DISCUSSION

The equilibrium adsorption of the poly(vinylpyridines) on both cellulose fibers and titanium dioxide is appreciably higher than that of the polyacrylamides discussed earlier.<sup>1</sup> This suggests that the dipolar interaction of the heterocyclic rings with surface hydroxyls is stronger than the hydrogen bonding of the polyacrylamides. The retention and coflocculation studies at pH 3.8 are, in general, analogous to the results found with polyacrylamides. Thus, suspensions of fibers are weakly flocculated whereas pigment suspensions are stabilized: mixed suspensions are coflocculated in a manner generally similar to the retention results.

TABLE V  
Pigment Retention and Sheet Opacity

TiO <sub>2</sub> retained, %	Sheet opacity, % contrast ratio	Polymer	Applied polymer, mg/g fiber	pH
92.7	96.1	P4VP-3	0.79	3.8
92.6	96.0	P4VP-2	0.81	3.8
92.5	96.0	P4VP-2	1.40	3.8
91.2	94.9	P2VP	1.39	3.8
90.7	95.0	P2VP	0.83	3.8
89.8	95.3	P2VP	0.42	3.8
89.5	95.3	P4VP-3	1.38	3.8
89.1	94.8	P4VP-1	1.25	6.5
87.4	94.6	P4VP-1	0.82	6.5
87.3	93.9	P2VP	1.21	6.5
86.6	94.8	P4VP-3	1.25	6.5
86.2	94.9	P4VP-2	0.82	6.5
85.1	95.2	P4VP-2	1.23	6.5
84.3	95.1	P4VP-2	0.62	6.5
84.0	94.6	P2VP	0.81	6.5
83.9	94.8	P4VP-1	0.82	3.8
82.4	94.2	P4VP-1	1.39	3.8
82.0	94.6	P4VP-3	0.82	6.5
81.9	95.0	P4VP-2	0.41	3.8
80.8	94.7	P4VP-1	0.62	3.8
79.5	94.5	P4VP-1	0.63	6.5
79.4	94.4	P2VP	0.62	6.5
77.9	94.5	P4VP-3	0.39	3.8
77.6	93.5	P4VP-3	0.61	6.5
72.4	93.6	P4VP-1	0.41	3.8
67.7	93.1	P2VP	0.21	3.8
47.6	90.5	P4VP-2	0.20	3.8
40.1	88.1	P4VP-3	0.21	3.8
39.4	88.0	P4VP-1	0.21	3.8
27.8	84.6	P2VP	0.85	6.6 <sup>a</sup>
25.6	84.2	P4VP-3	0.82	6.6 <sup>a</sup>
24.2	82.6	P4VP-2	0.82	6.6 <sup>a</sup>
24.1	81.0	P4VP-1	0.83	6.6 <sup>a</sup>
19.8	77.9	—	0	4.5
11.9	76.3	—	0	6.5
0	72.9	—	0	6.5

<sup>a</sup> Stock and polymer mixed at pH 6.6 before adding to sheet machine.

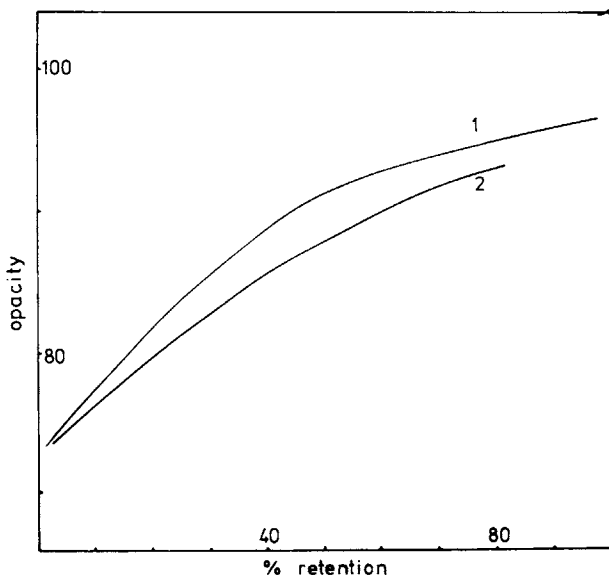


Fig. 8. Opacity (% contrast ratio) of dry sheet as function of titanium dioxide retention in presence of (1) poly(vinylpyridines), (2) polyacrylamides.

However, it is not clear from the measurements made with the poly(vinylpyridines) whether charge effects contribute to the observed behavior, since the observations made at neutral pH refer to rather special circumstances because of the insolubility of the polymer. Further, recent ionic equilibrium studies<sup>5</sup> suggest that the poly(vinylpyridines) are not significantly protonated at pH 3.8, the most acid condition used in the present study. In sheet formation, high retention at pH 6.5 is shown only if the retention aid contacts the stock suspension of fibers and pigment particles at acid pH; when precipitation of the polymer proceeds concurrently with sheet formation, the improvement in pigment retention is poor. On the other hand, Figure 3 shows a typical polymer flocculation of titanium dioxide at pH 6.5 which cannot result from precipitated polymer bringing down the suspended particles since such a process would not lead to restabilization at higher polymer loadings. Further, the coflocculation curves at pH 6.5 (Fig. 5) are roughly superposable on the pH 3.8 data if the polymer loading axis is shifted as if some 5 mg/g fiber were "wasted" at the higher pH. The sheet opacity at a given pigment retention does not depend on the pH conditions of sheet formation, which implies that the state of aggregation of the titanium dioxide is more or less invariant.

When judged in terms of sheet opacity at a given retention (Fig. 8), or by retention alone (Fig. 1), the poly(vinylpyridines) are rather better retention aids than the polyacrylamides. In the preceding paper,<sup>1</sup> we compared the proportion of pigment carried down in the coflocculation experiments with the retention in sheet formation and showed that the former quantity was consistently smaller. The same conclusion is made in the case of the poly(vinylpyridines), which give, at fixed percentage of pigment in the flocs in coflocculation, a marginally higher sheet retention.

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