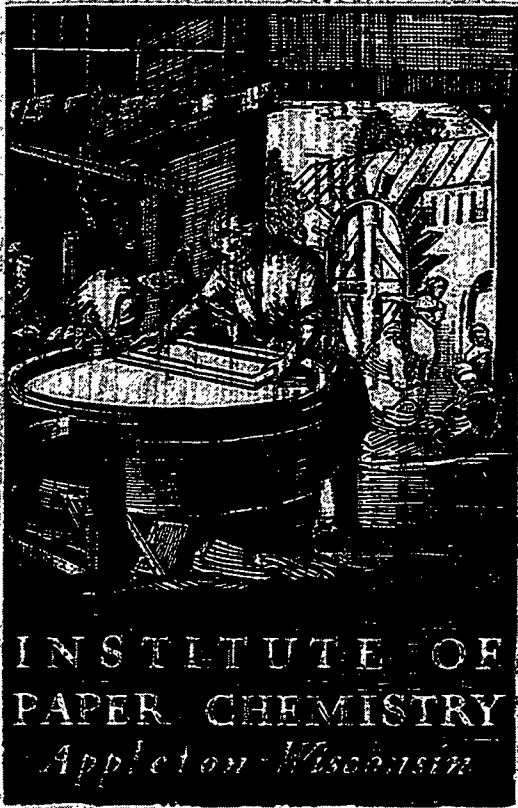


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**A FUNDAMENTAL STUDY OF THE MECHANISMS OF  
ACTION OF POLYMERS AS RETENTION AND  
DRAINAGE AIDS**

**Project 3276**

**Report Three**  
**A Progress Report**  
**to**  
**MEMBERS OF PROJECT 3276**

**April 4, 1977**

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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POLYMERS AS RETENTION AND DRAINAGE AIDS

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Report Three

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MEMBERS OF PROJECT 3276

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A FUNDAMENTAL STUDY OF THE MECHANISMS OF ACTION OF  
POLYMERS AS RETENTION AND DRAINAGE AIDS

SUMMARY

The use of polymers as retention and drainage aids can solve some environmental, operational, and production problems without a large capital expenditure. This progress report details our further studies of the interaction of the polymers with the various components of the furnish. The information will ultimately be used by the papermaker to operate his system more efficiently.

The role of fines level and degree of fibrillation on the retention process were examined using the Rapid Mixing Apparatus. Increased fibrillation was correlated with increased retention. The amount of fines had no effect on the maximum retention obtainable with a given polymer. However, the presence of fines was shown to increase the time rate of development of retention.

Filler clay was retained well when either low or high charge density, high molecular weight cationic polymers were used. Clay retention developed more rapidly in time than did  $TiO_2$  retention and was independent of the presence of pulp fines. Polymer bridging was suggested to be the major retention aid mechanism.

To learn which of the various components in a paper furnish might inhibit the action of retention aids, we examined several of the additives individually. Alum or overdoses of cationic starch reduced retention due to competition of these species with the cationic retention aids for adsorption sites. A hemicellulose fraction increased the polymer demand when a high charge density polymer was used, but provided a beneficial effect when a high molecular weight, low charge density polymer was used. Hypochlorite-oxidized starch (2% add-on) drastically reduced the retention at a given polymer dosage, and its effects could be nullified by an

eight-fold increase in dosage. This behavior was shown to be a result of charge interactions of the anionic starch. Pearl cornstarch reduced retention slightly by formation of a protective colloid around a portion of the pigment.

Although variations in retention behavior were noted among a bleached softwood kraft, an unbleached softwood kraft, a bleached hardwood kraft, and a stone groundwood (pine), the broad features were similar and the maximum levels of retention were similar. Thus the particular typical retention aids employed would appear to be applicable to a broad range of furnishes.

A modification of the Rapid Mixing Apparatus was used to measure simultaneously the retention and drainage characteristics of a beaten, classified pulp and a groundwood pulp. For the former the largest increases in drainage occurred at strongly positive values of the zeta potential and were attributed to a polymer bridging mechanism. The drainage rate for the groundwood pulp was enhanced only in the region of zero zeta potential, suggesting a charge neutralization and fines flocculation mechanism.

## INTRODUCTION

When a polymer retention aid is added to the pulp stream shortly before the paper machine headbox, a series of complex interactions occur. The polymer molecules will be transported by Brownian diffusion and turbulent convection to the various surfaces available: fiber, pulp fines, and filler. At these surfaces the polymer will be adsorbed if the interactions between the macromolecule and the surface are favorable. For cationic retention aids the interaction with the surfaces will include electrostatic contributions in addition to the Van der Waals forces, and the adsorption can be characterized as virtually irreversible. The importance of even distribution of the polymer to the furnish is obvious.

The retention aid can also interact with other dissolved species (usually those bearing negative charges). This increases (1) the overall cationic demand of the furnish which may be defined as the amount of cationic polymer to bring the surfaces to a zeta potential of zero.

Subsequent to the polymer adsorption step the colloidal and larger particles can form aggregates upon collision. The mechanism of flocculation induced by the adsorbed polymer has been variously attributed to bridging (2), charge neutralization (3), and electrostatic patch formation (4) or combinations of these. For the flocculation of colloids by high molecular weight polyelectrolytes of opposite charge both bridging and charge interactions have been shown (5) to be important. Bridging is also a possibility with low molecular weight polymers when the colloid particle size is correspondingly small (6).

The efficiency of the collisions leading to aggregation depends upon polymer parameters (molecular size and charge), surface parameters (particle size and surface charge density), and parameters of the medium which affect the electrical

double layer of the particles and the end-to-end extension of the polymers (ionic strength and pH). The collision efficiency must be high enough so that retention will occur within the time scale allowed by the paper machine operating parameters. Two factors can reduce this efficiency. An overdose of cationic polymer can reverse the charge on the normally negatively-charged surfaces of the pulp leading to strong repulsion between approaching particles. Secondly, the phenomenon of steric stabilization (or protective colloid) (7) can prevent the natural aggregation of the particles and possibly also inhibit the adsorption of the polymer. The action of various starches as protective colloids is well known, and their deleterious effect on filler retention has long been recognized (8,9).

This project was undertaken to gain a better understanding of the complex interactions between the polymers and the pulp and filler surfaces which culminate in filler retention in the paper sheet. In previous reports (5,10) it was shown that the major parameter affecting retention and performance was the latter's molecular weight. For polymers with moderate molecular weight, maximum retention was found at a dosage corresponding to that necessary to bring the stock to a zeta potential near zero. At higher dosages the reversed charge on the particles produced poorer retention. For polymers with high molecular weight ( $\geq 10^6$  daltons) good retention was also found for polymer concentrations near that necessary to reduce the zeta potential of the furnish to near zero. However, in this case equally good retention can also be achieved at much larger dosages where the zeta potential of the stock is strongly positive ( $>+20$  mv). This behavior was attributed to the possibilities for bridging associated with the longer polymer chain lengths. Here, also, it was found that a high molecular weight polymer with low charge density produced higher filler retention than a corresponding polymer with high charge density. It was suggested that the flatter surface configuration of the highly charged polymer allowed



fewer possibilities for bridging with concomitant lower retention. Experiments at very short contact times (10) provided support for the phenomenon of "nonequilibrium flocculation" as enunciated by Gregory and Sheiham (11). In the latter's hypothesis even when the final equilibrium configuration of the adsorbed polymer is relatively flat, extensive bridging is possible during the early stages of polymer adsorption if the colloid particle concentration is high enough. In the retention studies mentioned above part of the enhanced retention provided by high compared to moderate molecular weight polymers (both with high charge density) can be attributed to the effects of nonequilibrium flocculation.

Pulp fines were found to accelerate the development of retention. At the same time the polymer used must be a good retention aid for the pulp fines as well as for the filler so that the pigment attached to the fines is not lost to the white water. Again high molecular weight polymers were found to be much better retention aids for the fines than were those of moderate molecular weight.

The role of polymers as drainage aids was also examined in the previous reports (5,10). For a softwood bleached kraft pulp the major function of the polymer in improving drainage was to reduce the hydrodynamic specific surface area of the fibers. The polymer dosages required for maximum improvement suggested a bridging mechanism as the mode of interaction of the polymer with the fibers. The amount of drainage enhancement was independent of the pulp fines level (range 0-15% fines), implying that polymer flocculation of the fines was not significant for this system.

Part of the studies discussed in the present report parallel corresponding work in Project 3245, "Improving Retention of Particulate Matter When Employing Recycled White Water." In Project 3276 the emphasis is on the role of polymers as retention aids while the thrust of Project 3245 concerns increasing our understanding

of the changes in retention behavior associated with white water recycling. To facilitate intercomparison of the results of the two projects, a common pulp was used. Although different approaches and techniques were used in the two projects, the results are complementary.

In the first part of this report the effects on filler retention of pulp characteristics, headbox agitation, and interactions with other common furnish components are examined.

The second part reports experiments on the simultaneous measurement of retention and drainage. The ability of representative polymers to improve both these properties is correlated with pulp type.

Finally, the work remaining will be outlined.

## FILLER RETENTION STUDIES

## EFFECTS OF FINES AND FIBRILLATION

Previous work (5) implied that the dominant factor controlling the level of retention possible when using a given retention aid was the amount of fibrillation of the fiber. Pulp fines were shown to increase the time rate of attainment of the maximum retention presumably by increasing the collision frequency. It was suggested on limited evidence that the pulp fines had little effect on the time independent level of retention. The present experiments were designed to place these conclusions on a firmer basis and to provide information on pulps which might be considered typical from the viewpoint of degree of refining.

A softwood bleached kraft was beaten to several levels of freeness as described in a previous report (10). Portions of the beaten pulps were then classified. The Canadian standard freenesses were reported (10). Filtration resistance measurements at constant flow rate were carried out as described previously (10) and the results were analyzed to yield the hydrodynamic specific surface area  $\frac{S}{w}$  and hydrodynamic specific volume  $\underline{v}$ . These parameters for the various pulps are listed in Table I.

TABLE I

## PULP PARAMETERS FROM CONSTANT RATE FILTRATION MEASUREMENTS

Pulp	$\frac{S}{w}$ , cm <sup>2</sup> /g	$\underline{v}$ , cm <sup>3</sup> /g	CSF, ml
No. 1 whole	11,100	2.61	635
No. 2 whole	17,200	2.65	435
No. 3 whole	23,500	2.81	340
No. 4 whole	35,200	2.90	195
No. 1 classified	8,100	2.23	735
No. 2 classified	10,800	2.41	685
No. 3 classified	13,900	2.54	605
No. 4 classified	16,750	2.57	515

The filler retention behavior of the four whole pulps was examined using the Rapid Mixing Apparatus (RMA) (10) at a contact time of 40 sec and 5% TiO<sub>2</sub> based on the o.d. pulps. This time has been previously found (10) to be sufficient to reach maximum retention with whole pulps. Various concentrations of the fully quaternized, high molecular weight polymer Q100 (polymethacryloxyethyl trimethylammonium methosulfate) were utilized. The results are presented in Fig. 1 as percent of filler retention  $\bar{R}$  against the logarithm of the polymer concentration. Individual data points are omitted in the interests of clarity. There is only a small difference in retention among the pulps at low polymer dosages. Above 0.02% the results diverge greatly with a difference of greater than 20% in retention between the unbeaten pulp (No. 1) and the most highly refined (No. 4). As found previously for some classified pulps (5), the pulp containing the least fines exhibits two maxima. These were attributed (5) to two different mechanisms of retention aid action: charge interaction at the lower concentrations and bridging at the higher ones. For all the present pulps there exists a broad concentration domain where good retention can be expected. Before drawing conclusions with respect to the relative roles of fines and surface fibrillation on retention, we will describe two other sets of experiments.

The effect of fines and fibers on the retention process as mirrored by their separate contributions to the hydrodynamic specific surface area is examined next. Three pulps having approximately the same surface area  $\bar{S}_w$  were treated with Q100 in the RMA. They were the highly refined No. 4 classified pulp containing very few fines ( $\bar{S}_w = 16,750 \text{ cm}^2/\text{g}$ ), the slightly refined No. 2 whole pulp containing a small amount of fines ( $\bar{S}_w = 17,200 \text{ cm}^2/\text{g}$ ), and a mixture of the unbeaten, classified pulp No. 1 (95%) with 5% of No. 4 fines ( $\bar{S}_w = 17,200 \text{ cm}^2/\text{g}$ ). The latter figure was calculated from the value for the classified pulp (8,100 cm<sup>2</sup>/g) and that (5) for the fines (190,000 cm<sup>2</sup>/g) assuming additivity by weight fraction. The retention results

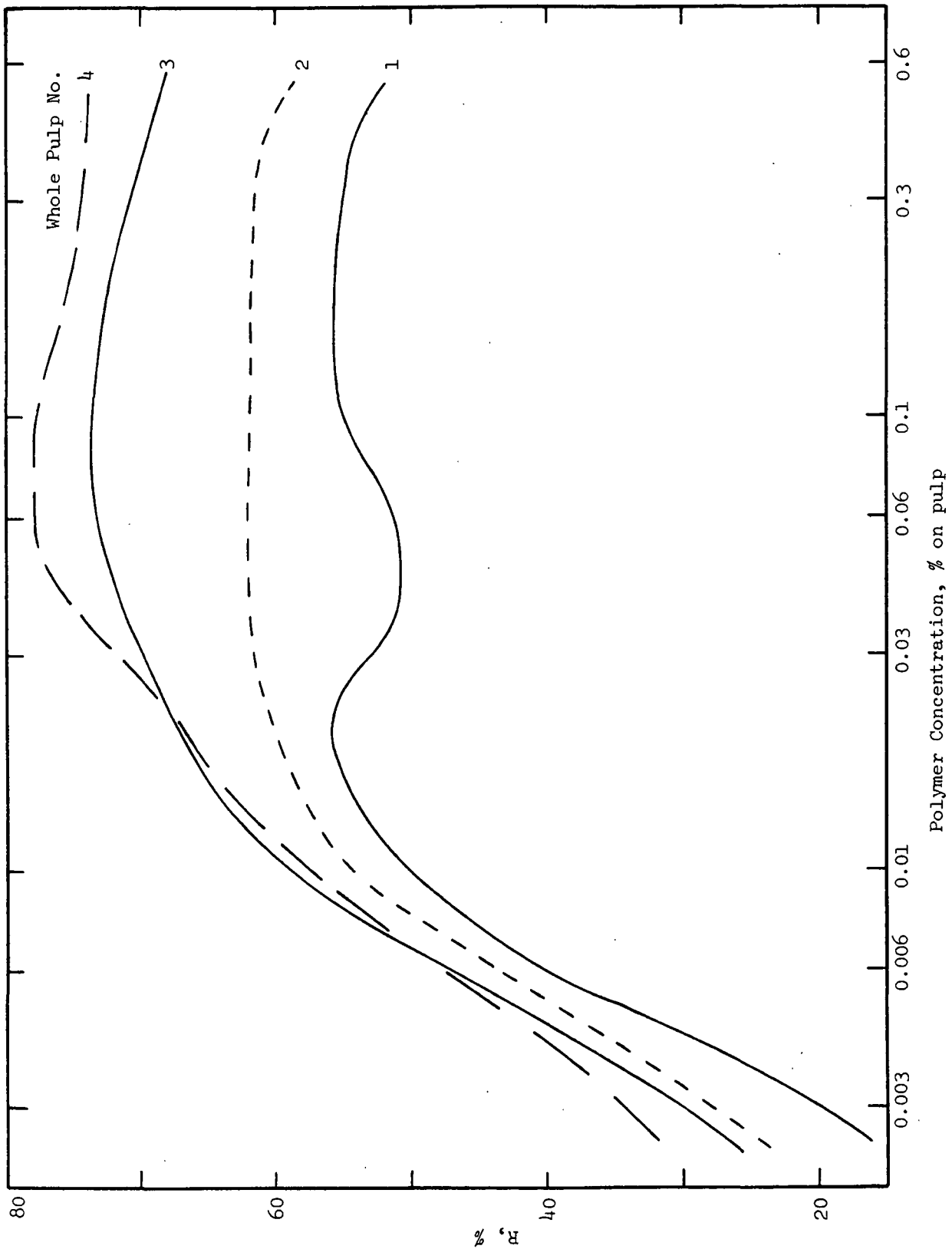


Figure 1. Dependence of TiO<sub>2</sub> Retention on Pulp Refining. Freenesses are Listed in Table I.  
Polymer: Q100. Contact Time: 40 Sec

at a contact time of 40 sec are presented in Fig. 2. The pulp with the highest degree of surface fibrillation attains the highest retention. However, part of the differences noted may reflect the loss to the white water of  $TiO_2$  attached to unretained fines. The reason the maximum value of retention for No. 4 classified is about 10% less than that for No. 4 whole (Fig. 1) may be twofold. The contact time of 40 sec may be insufficient to allow attainment of the maximum (5) and there is some evidence (10) that partial irreversible drying resulting in decreased fibrillation occurred during the classification process.

The final set of experiments involved the preparation of a series of pulps with increasing fines contents. Classified pulp No. 3 was mixed in ratios of 100/0, 95/5, 90/10, and 85/15 with No. 4 fines. The corresponding (calculated) values for  $\underline{S}_w$  were 13,900, 22,700, 31,500, and 40,300  $cm^2/g$ . Thus the degree of fibrillation representing that of a moderately well-refined pulp was held constant. (One could alternatively view this set of experiments as modeling a set of systems with increasingly larger amounts of white water recycling.) Two polymers, Q100 and T100 (a high-charge density polyelectrolyte of moderate molecular weight), were used separately as retention aids.

The results at contact times of 40 sec are shown in Fig. 3 and 4 for T100 and Q100, respectively. The salient feature in both plots is the virtual independence of the maximum level of retention on the quantity of fines in the system. This, together with the other evidence above, strongly suggests that it is the amount of fiber surface fibrillation as proposed at the beginning of this section rather than the fines content that determines the maximum retention possible.

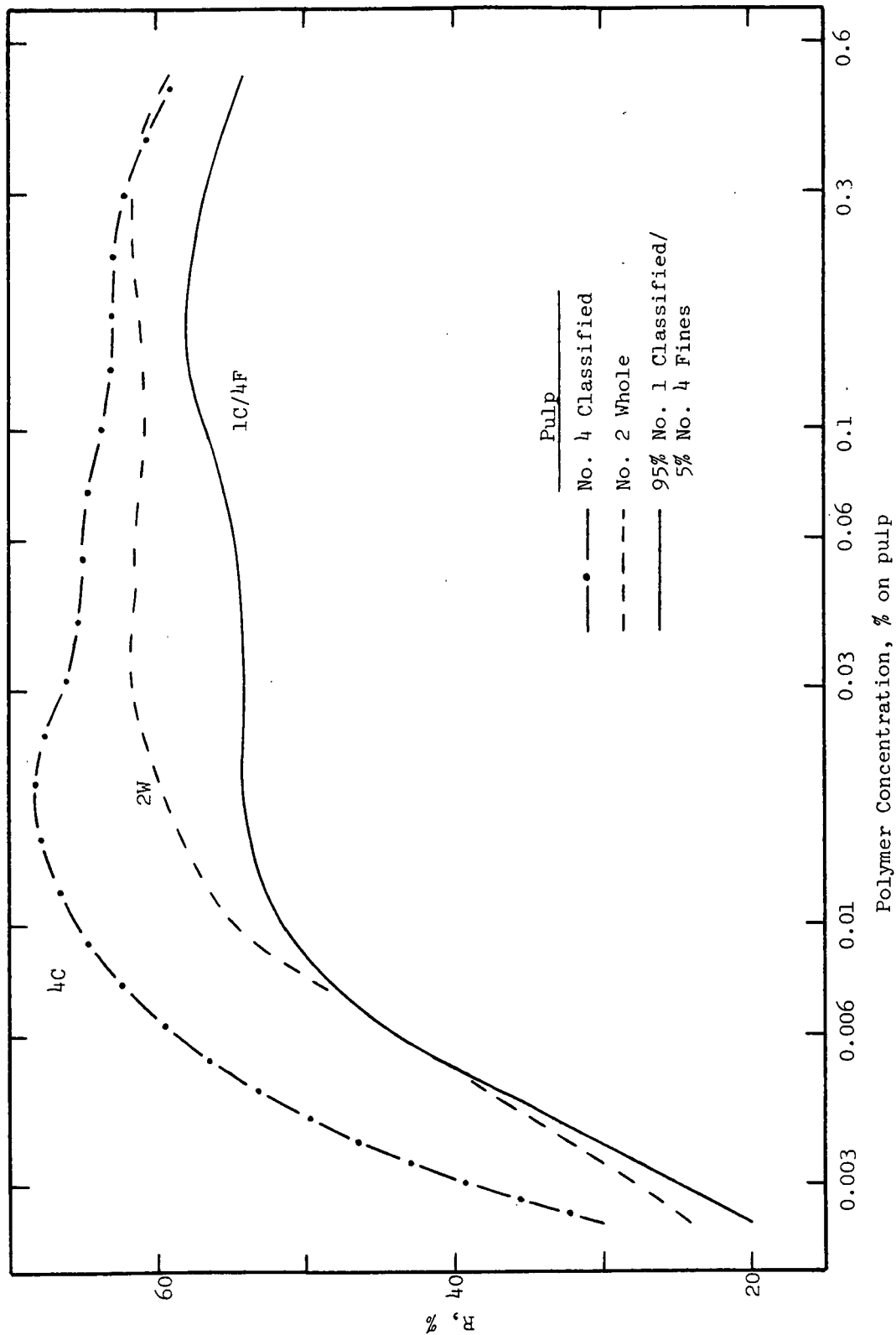


Figure 2. Dependence of  $TiO_2$  Retention on Amount of Fines and Fibrillation at Constant Hydrodynamic Specific Surface Area. Polymer: Q100. Contact Time: 40 Sec

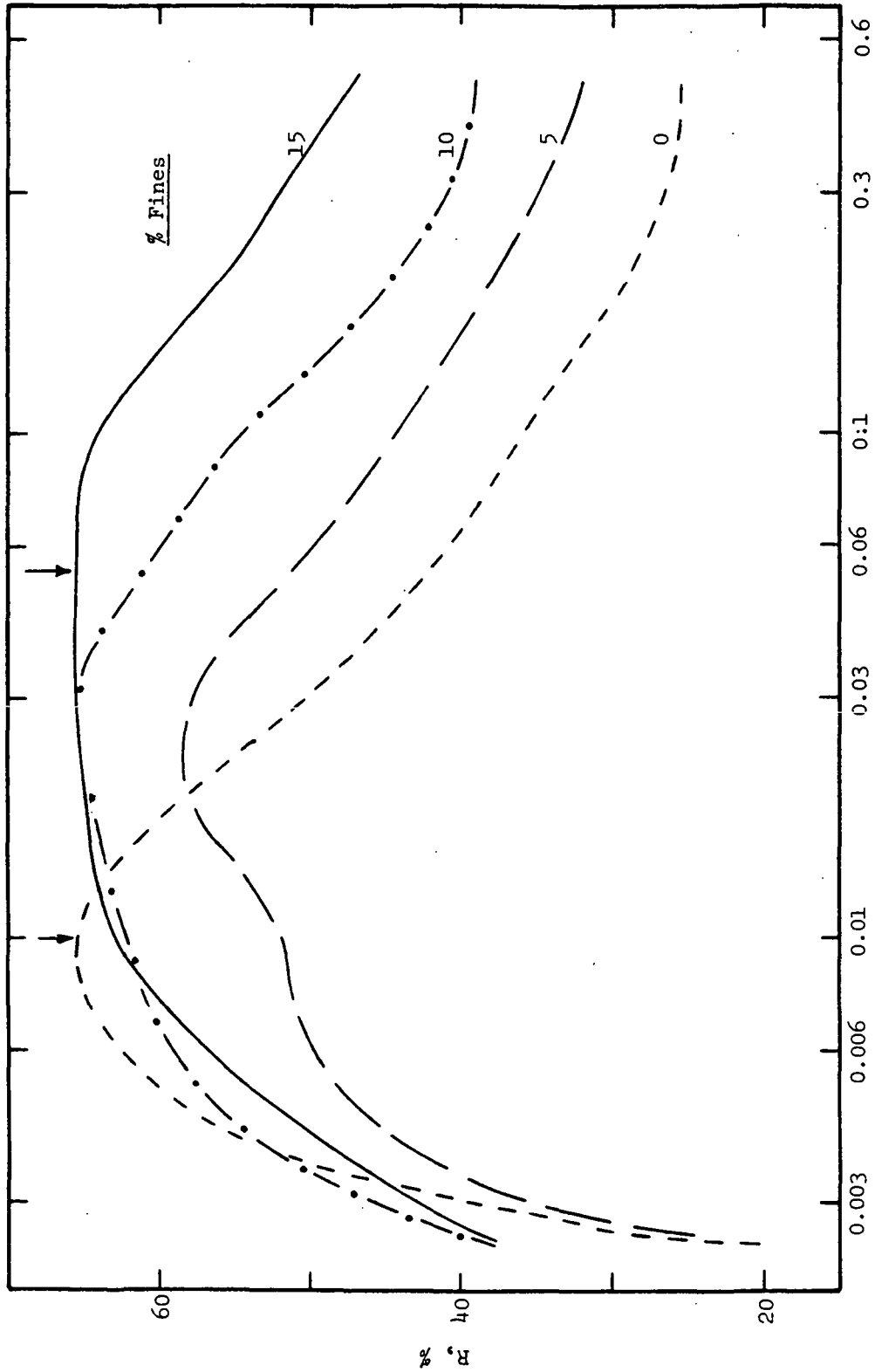


Figure 3. Effect of Amount of Pulp Fines on  $TiO_2$  Retention. Polymer:  $TiO_2$ . Contact Time: 40 Sec



For the experiments using T100 the major effect of the fines is to increase the range of good retention. The concentrations to achieve zero zeta potential for the samples containing 0 and 15% fines are shown by the arrows in Fig. 3. The addition of 15% fines increases the cationic demand by a factor of about five. As noted previously (5) for this moderate molecular weight polymer, retention begins to decrease as the charge is reversed due to overdosage. It is perhaps remarkable that the pulps with 0, 10, and 15% fines exhibit nearly identical retention at a polymer dosage of 0.01%. At this point the zeta potential varies from zero for no added fines to -17 mv for 15% fines. An electrostatic patch mechanism would seem to be the only likely explanation for the good retention found in the latter case with this polymer of moderate chain length.

The results in Fig. 4 for treatment with Q100 do not exhibit the rapid decrease in retention with increasingly positive zeta potential as observed with T100 above. There is, indeed, little difference among the four furnishes over the entire concentration range, reinforcing the view that fibrillation is the controlling factor in filler retention. The values for retention for the pulp with no added fines may be a little lower than those for the other pulps, particularly at moderate to high polymer dosages. This is probably a result of insufficient contact time to allow the maximum retention to be reached as shown in previous work (5).

The maximum retention found for these pulps using Q100 is about 8% greater than when T100 is used. This undoubtedly reflects the greater possibilities for bridging associated with the longer chain length — particularly "nonequilibrium flocculation" (10).

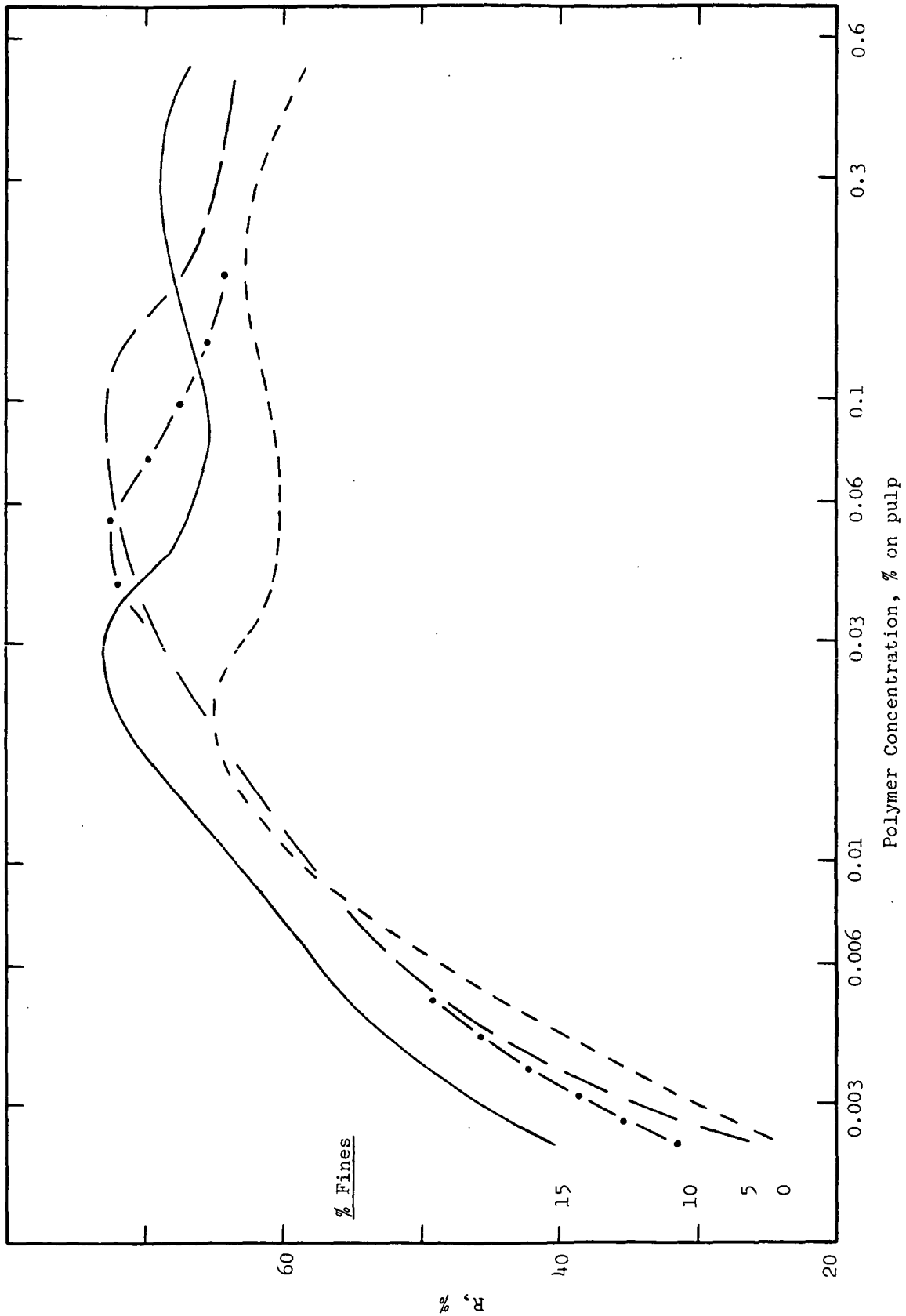


Figure 4. Effect of Amount of Pulp Fines on TiO<sub>2</sub> Retention. Polymer: Q100. Contact Time: 40 Sec

## EFFECT OF HEADBOX AGITATION

In a previous report (10) a limited study of headbox agitation on retention was performed using a low charge density, moderate molecular weight polymer. Only minimal effects were noted. In view of the drastic effects of agitation reported (12-14) when using the Britt "drainage jar," it was desirable to investigate the effect of this parameter in more detail.

The agitation in the RMA deckle box was achieved as described previously (10) using an ordinary 3-bladed propellor driven at rates of 200, 500, or 1000 rpm. A contact time of 40 sec was used with No. 3 whole pulp treated with various concentrations of either T100 or Q100. As before (10), the agitation was discontinued 1-2 sec prior to applying the suction to allow the swirling to subside and assure good formation.

The results are shown in Fig. 5. (Note the shift in ordinates for the two polymers.) The changes found in retention with increased agitation are small as noted previously (10). At those concentrations where retention increases with an increase in agitation rate, it can be postulated that 40 sec contact time was insufficient at the lower rate to achieve maximum retention. Increasing the stirrer speed increases the particle collision rate. It must be concluded that the 1-2 sec subsidence time is sufficient to recover any retention lost during the agitation for the samples with T100. Similar recoveries have been found previously (14,15) for some polymers. The only clear case of decreasing retention with increasing agitation is for the samples at concentrations of Q100 between 0.01 and 0.1%. The decrease may be due to insufficient recovery time (15) or may be a real effect occasioned by polymer reformation during agitation (14,16). In the light of the low magnitude of the changes noted the studies were pursued no further. It is possible that

more intense agitation (14) than available with the present set-up would lead to larger decreases in retention.

#### COMPARISON OF CLAY AND $TiO_2$ RETENTION BEHAVIOR

Previous work on this project has been concerned with the retention of filler grade  $TiO_2$ . Because many paper mills use clays as fillers either alone or in conjunction with  $TiO_2$ , it was considered important to expand the study to include the former. The goal here is to determine the extent to which information generated using the  $TiO_2$  system can be applied to clay systems. For most of the experiments a filler grade clay, Georgia Kaolin WPSD, was used at an addition level of 10% based on the o.d. pulp (see Appendix). This material had been used previously (17) on Project 3245 and had a median particle size of about 1.6  $\mu m$  according to the manufacturer. For confirmation some experiments were also carried out using Klondyke KWW (Englehard Minerals and Chemicals Corporation). As might be expected from the similar particle size distribution of the two materials, the retention behavior was similar.

The results for experiments using either T100, Q100, or Q5 with No. 3 whole pulp and WPSD clay are illustrated in Fig. 6. A number of features are of interest here.

1. The time dependent development of retention is much more rapid for clay than for  $TiO_2$ . (Compare the results here for Q100 with those in Fig. 1, Progress Report Two. The other two polymers, Q5 and T100, also show a similar time dependence for  $TiO_2$  retention to that in Fig. 1.)

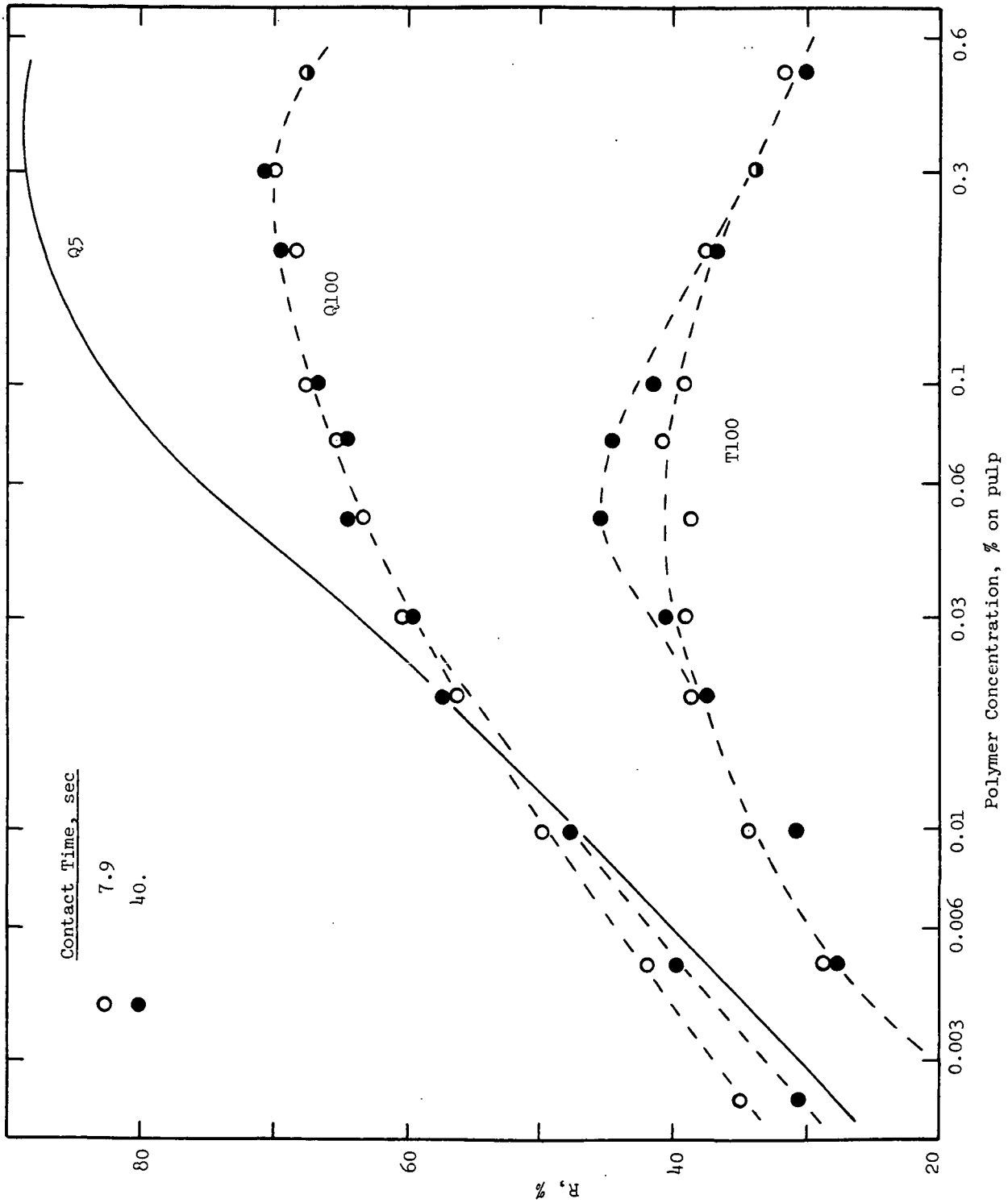


Figure 6. Dependence of Clay Retention on Polymer Type and Contact Time. Curve Shown for Q5 is at a Contact Time of 40 Sec

2. For  $\text{TiO}_2$  (see Fig. 11 of Progress Report Two), the high molecular weight, low charge density polymer Q5 provides about 10% greater retention near the maximum than does the high charge density Q100. For clay the difference of 18% retention between the two polymers is even more dramatic.

3. For Q100 and Q5 the level of retention for clay at a particular polymer dosage is within 10% of that for  $\text{TiO}_2$  at the same dosage.

4. In contrast, except for large polymer dosages, the retention level for clay using T100 as the retention aid is much less than that for  $\text{TiO}_2$ . For example, the corresponding maxima are 45 and 62%, respectively.

Before commenting further on these results, we will adduce two additional pieces of information. First, the retention of clay by No. 4 classified pulp ( $\underline{S}_w = 16,750 \text{ cm}^2/\text{g}$ ) using Q100 was studied. The results can be superimposed on those for Q100 with No. 3 whole pulp ( $\underline{S}_w = 23,500 \text{ cm}^2/\text{g}$ ) presented in Fig. 6 over the whole polymer concentration range. Also, in agreement with the results of Fig. 6, there is little increase in retention (<5%) between contact time of 7.9 and 40 sec for clay and the classified pulp. This is in strong contrast to the results for  $\text{TiO}_2$  with classified pulps. (Compare the time dependence in Fig. 2, 5, 6-7, 12-13, and 14 of Progress Report Two for classified pulps.)

Finally, a more detailed examination of the time dependent development of retention of clay was carried out. Both moving wire and sheet mold modes were used with No. 3 whole pulp, 10% WPSD clay, and 0.1% Q100. The latter concentration provides near maximum retention for both  $\text{TiO}_2$  and clay. The results are presented in Fig. 7 along with comparable values for  $\text{TiO}_2$  (from Fig. 9, Progress Report One).

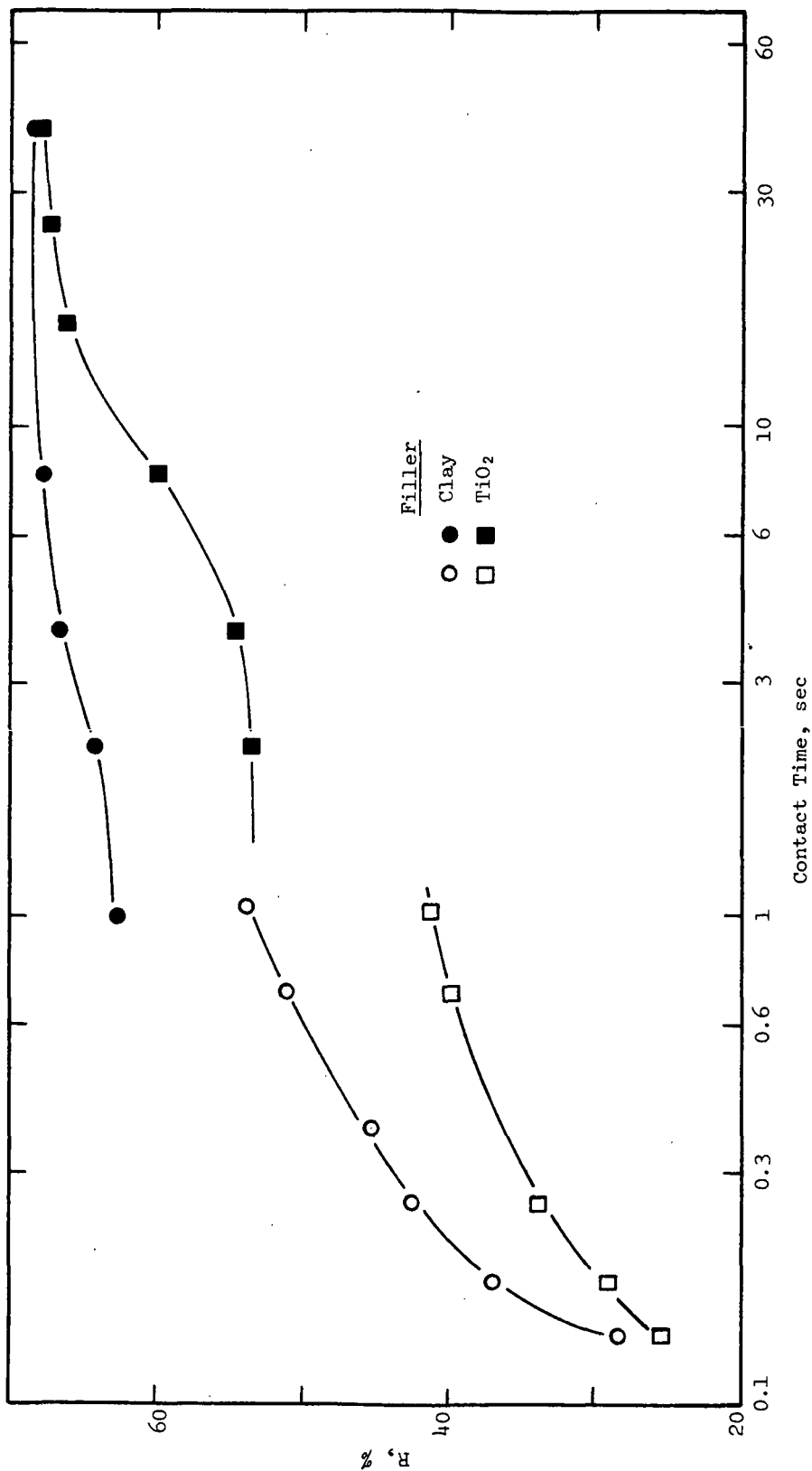


Figure 7. Development of Retention with Contact Time in RMA. Open Symbols: Moving Wire Mode. Filled Symbols: Sheet Mold Mode. Polymer: Q100. Polymer Concentration: 0.1% on Pulp

It will be recalled that the dichotomy between the results from moving wire and sheet mold modes results from the different drainage forces present in the two instances. Apparently, clay retention develops much more rapidly and is essentially complete after 2-3 sec whereas a sizeable fraction of the  $TiO_2$  retention develops between 4 and 20 sec. Eventually both fillers achieve about 68% retention.

In summary the evidence shows that  $TiO_2$  retention -

1. occurs over an extended time scale,
2. is accelerated by the presence of pulp fines, and
3. can reach a moderate level ( $\sim 60\%$ ) by use of a moderate molecular weight, high charge density polymer (T100).

Clay retention -

1. occurs very rapidly for all polymers examined,
2. is independent of the presence of fines (and possibly  $\frac{S}{W}$ ), and
3. is only fair ( $\sim 45\%$ ) with T100.

Both clay and  $TiO_2$  retention -

1. increase with increasing retention aid molecular weight, and
2. are highest with a high molecular weight, low charge density retention aid.

Collectively, these findings suggest that  $TiO_2$  can be retained by either a charge interaction or by bridging. Clay, on the other hand, would appear to be mainly retained by a polymer bridging mechanism. Part of the high level of clay retention at the very short times may be by a simple sieving mechanism since some of the particles are as large as 15  $\mu m$ . The absence of a dependence of clay retention on fines can be contrasted with an earlier study (17) which used alum as the retention aid. In that work it was suggested that the clay was primarily



retained onto pulp fines, which were themselves subsequently retained by the fibers. Apparently, the bridging mechanism available to polymers does not require the presence of pulp fines for efficient retention.

#### EFFECTS OF OTHER COMMON FURNISH COMPONENTS ON RETENTION

In order to isolate the effects of various pulp and polymer parameters on retention, we have heretofore considered only relatively "pure" systems. In the paper mill, of course, such systems are not found. It is often the other components, whether added intentionally or arriving as part of the raw materials, which cause problems in filler retention (18). Variation in the quantities of these other components is the likely cause of many system upsets. One of the major objectives of this project is (10) "to determine those major parameters which cause variability in the effectiveness of polymers as retention or drainage aids." As discussed in the Introduction these minor components can either interact directly with the polymer, resulting in an increased polymer demand by the system, or inhibit the retention mechanisms of the polymer, as by protective colloid formation.

In this report several common additives are studied for their effect on the ability of typical retention aids to produce good retention of  $TiO_2$  efficiently. To facilitate the correlation of the present work with that of Project 3245 on recycling, the pulp previously used with the latter project was employed. This was a bleached kraft northern softwood pulp beaten to 445 ml CSF and possessing a hydrodynamic specific surface area of  $22,200 \text{ cm}^2/\text{g}$  (17). It is very similar in composition and retention behavior to the No. 3 whole pulp used above and in previous reports on this project (5,10). The composition, preparation, and method of addition of the various components to the furnish are described in detail in the Appendix. The two high molecular weight retention aids, Q5 and Q100, with low and high charge density,

respectively, were employed at contact times of 7.9 and 40 sec in the RMA. The effect of most of the additives was to decrease the dependence of retention on contact time. (The lone exception was the unmodified starch for which the time dependence was about the same as that found for the pulp alone.) Therefore, to reduce confusion in the plots and because we feel the longer time more representative of mill conditions, only the results at 40 sec will be discussed. The pH of the furnish and polymer solution were adjusted to 5.0 with  $H_2SO_4$  or NaOH except for the system with rosin sizing (pH = 4.7). To allow facile interpretation, only one additive was introduced at a time.

#### Hard Water

An artificial hard water was used for stock preparation, dilution, and polymer solution. The composition is listed in the Appendix. Sulfate, calcium, magnesium, sodium, and chloride ion are present. The hardness is 435 ppm as  $CaCO_3$ . Two effects might be anticipated. The cationic polymers might bind the anions, particularly sulfate, thereby reducing the retention aid's effectiveness. Or, the various ions may merely act to compress the electrical double layer surrounding the various particles and thereby facilitate coflocculation (retention). The results are presented in Fig. 8 along with those for the base line system (distilled water). The interaction is seen to produce a positive effect with either of the polymers over the whole range of concentrations. The increase with hard water is especially marked at low polymer concentrations. Indeed, the retention with hard water and no polymer (56%) is equivalent to the addition of about 0.01% polymer to the system consisting of distilled water. The added ions act as a sensitizer (4) to reduce the polymer demand necessary to reach a given retention. The apparent mechanism is compression of the electrical double layer.

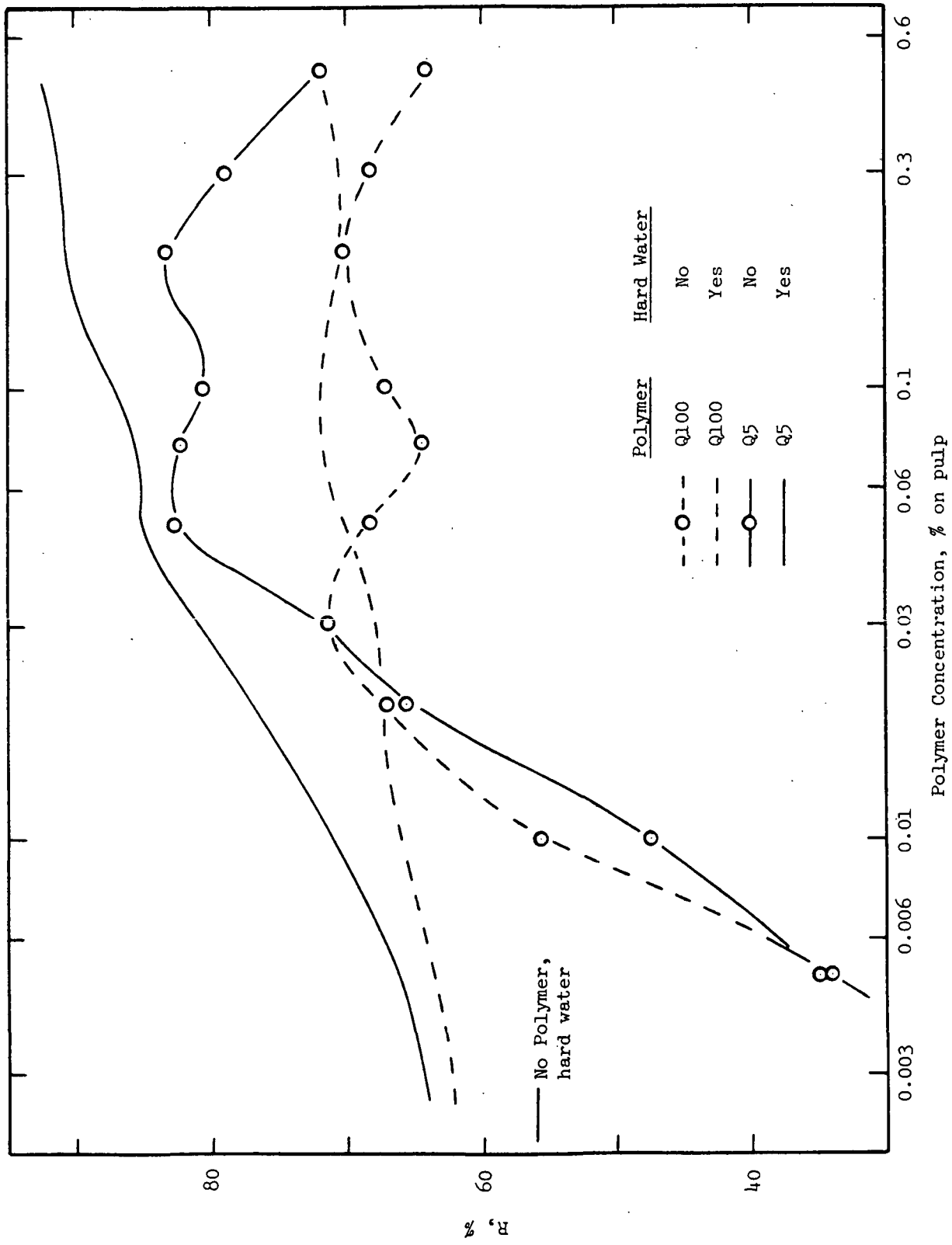


Figure 8. Comparison of TiO<sub>2</sub> Retention with Distilled and with "Hard" Water. Contact Time: 40 Sec

Hemicellulose

The addition of small amounts of a pine xylan to a suspension of micro-crystalline cellulose has been shown (1) to markedly increase the amount of cationic polyacrylamide necessary to reduce the (initially negative) zeta potential to zero. In Project 3245 it was found (19) that 0.1% of a hemicellulose prepared by a caustic extraction of a softwood kraft pulp reduced the retention of  $TiO_2$  from 72 to 46% when using 2.2% alum as a retention aid.

We report here the effect of this same hemicellulose preparation on the retention efficiency of Q5 and Q100. The details of the extraction process and the sugar analysis of the hemicellulose are given in the Appendix. The retention results are presented in Fig. 9. The base line data are the smoothed curves drawn through the distilled water system in Fig. 8. The behavior of the two polymers is rather different. For Q100 the addition of the hemicellulose appears to increase the polymer demand by a factor of about two, and the curve is correspondingly shifted. The maximum retention increases slightly. In contrast the interaction of Q5 with the hemicellulose increases the filler retention over the entire polymer concentration range. The results are particularly striking at concentrations  $\leq 0.01\%$  Q5 where prior addition of hemicellulose improves retention by 25-30%. The explanation of these intriguing data is not immediately apparent. The hemicellulose, a mixture of polymers containing anionic groups, may be specifically adsorbed on the  $TiO_2$  particles. The interaction between these "treated" particles and the Q5 polymer may lead to a particularly efficient method of retention. The balance of electrostatic charges would seem to be especially critical here since the high charge density polymer Q100 behaves entirely differently.

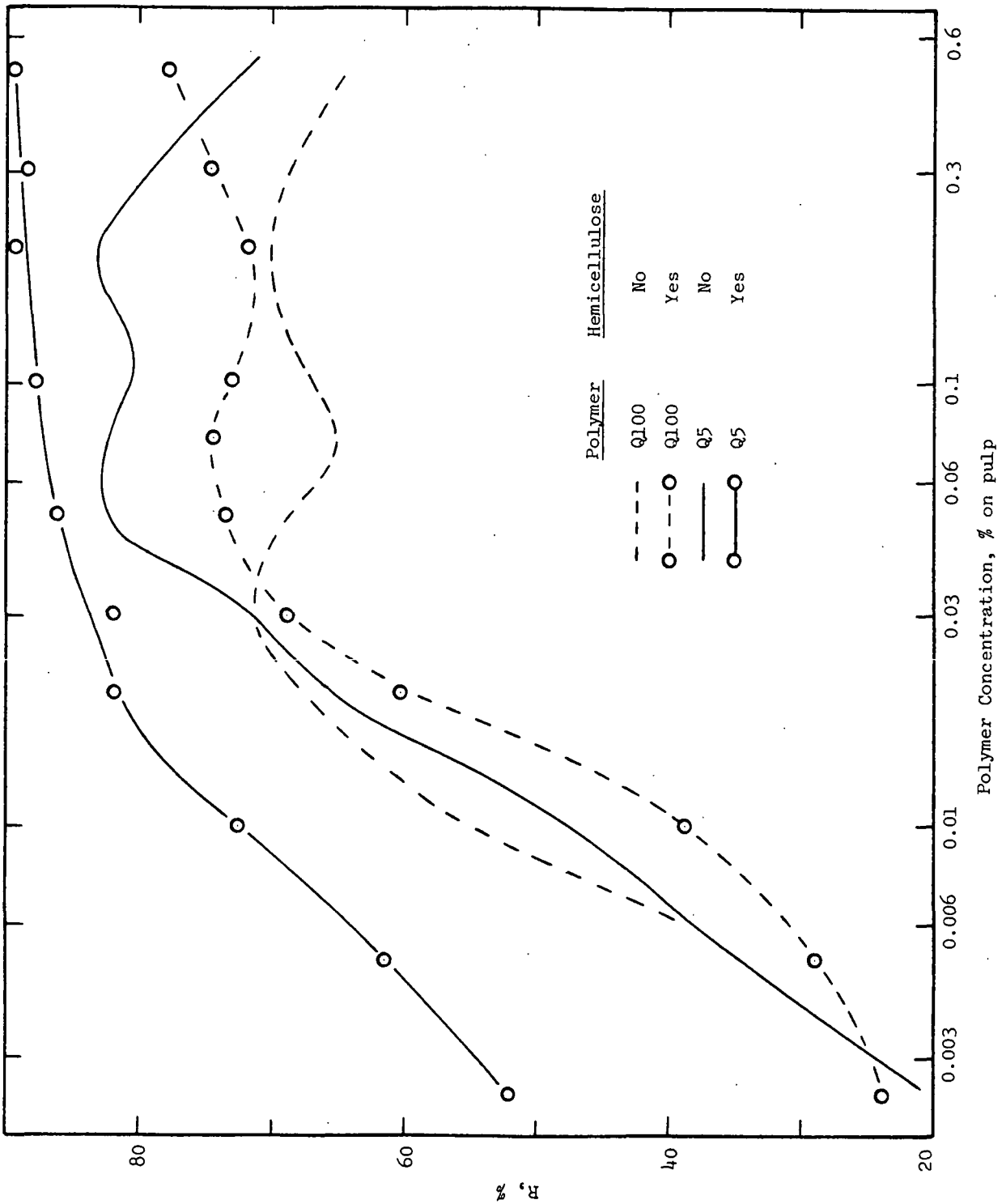


Figure 9. Effect of the Presence of a Hemicellulose Fraction (16% NaOH Extract) on TiO<sub>2</sub> Retention. Contact Time: 40 Sec

Alum

Papermakers' alum is added to the furnish in many mills for a variety of reasons: for pH adjustment, for rosin size retention, for filler retention, and for control of cationic demand (20). The interaction of alum with cationic polymers has been shown to produce either increases (21,22) or decreases (15,23) in retention compared to the system where only one of these materials is added.

For the present study 1% alum based on the o.d. pulp was added to the stock after the TiO<sub>2</sub> but before pH adjustment. This level of alum was previously found (17) to provide the maximum TiO<sub>2</sub> retention with this pulp. The results (Fig. 10) indicate the retention in the system alum/Q100 is only marginally better than that with alum alone. In the moderate range of polymer additions the system Q100 alone provides better retention than the combined system. The situation is similar with the alum/Q5 system. The combination provides somewhat better retention than alum alone but much less than the polymer alone. It is likely that competition exists between the hydrolyzed aluminum species and the cationic polyelectrolyte for adsorption sites on the TiO<sub>2</sub> and pulp. Since the alum is added first, it may be not surprising that the combined system acts more like that of alum alone. Work to elucidate these interactions is presently underway (24).

Rosin/alum Size

This experiment extends the complexity of the system by one more component. The preparation of the fortified size and the method of addition to the stock are described in the Appendix. One percent rosin and 1% alum were used with Q100. In Fig. 11 the curves for Q100, alum/Q100, and rosin/alum/Q100 are shown. The combination of rosin/alum/Q100 produces higher retention at moderate polymer dosages than does the alum/Q100 system. This is probably because the rosin combines with a sizeable fraction of the alum thereby reducing the competition between Q100 and

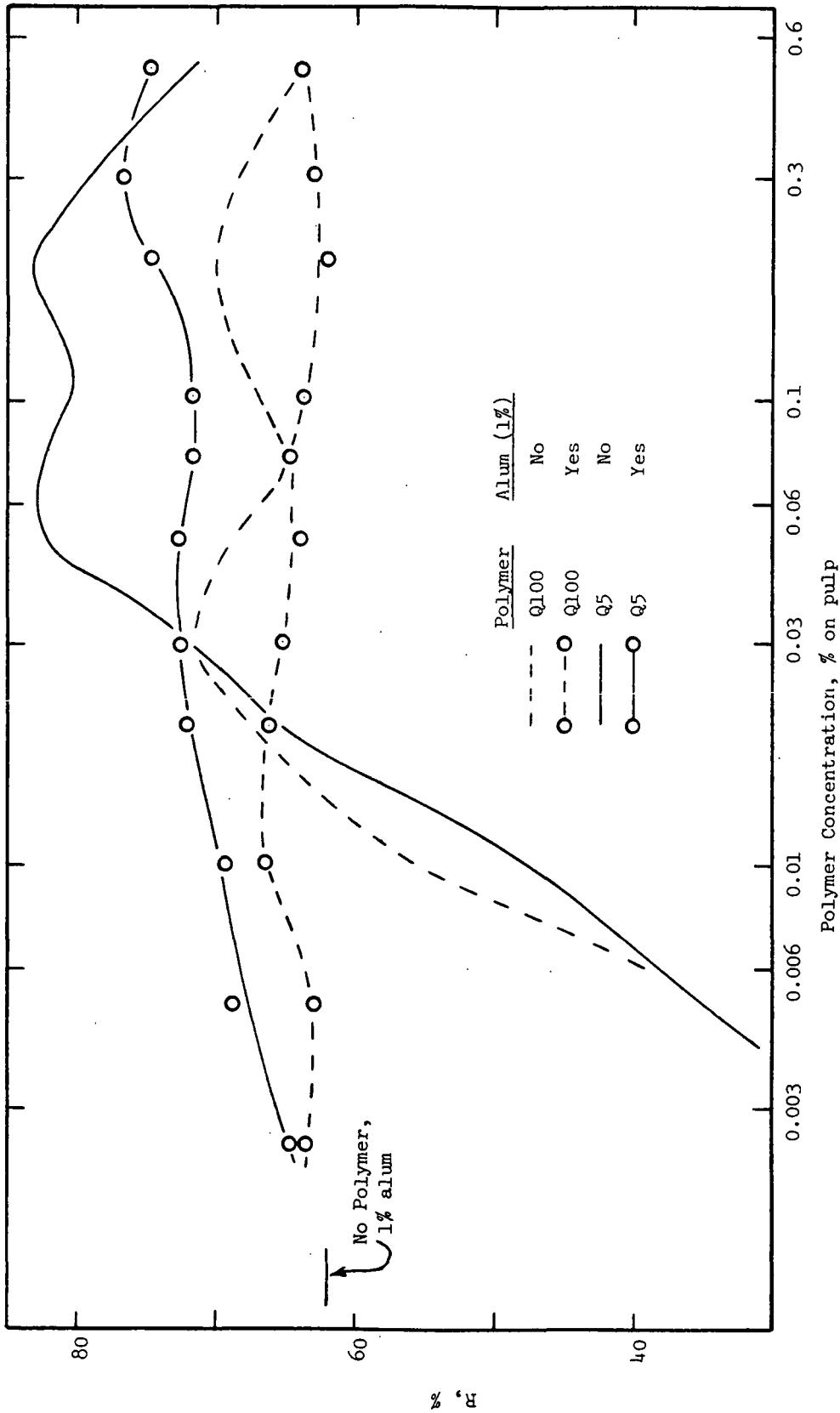


Figure 10. Influence of Alum on TiO<sub>2</sub> Retention Aided by Cationic Polymers. Contact Time: 40 Sec

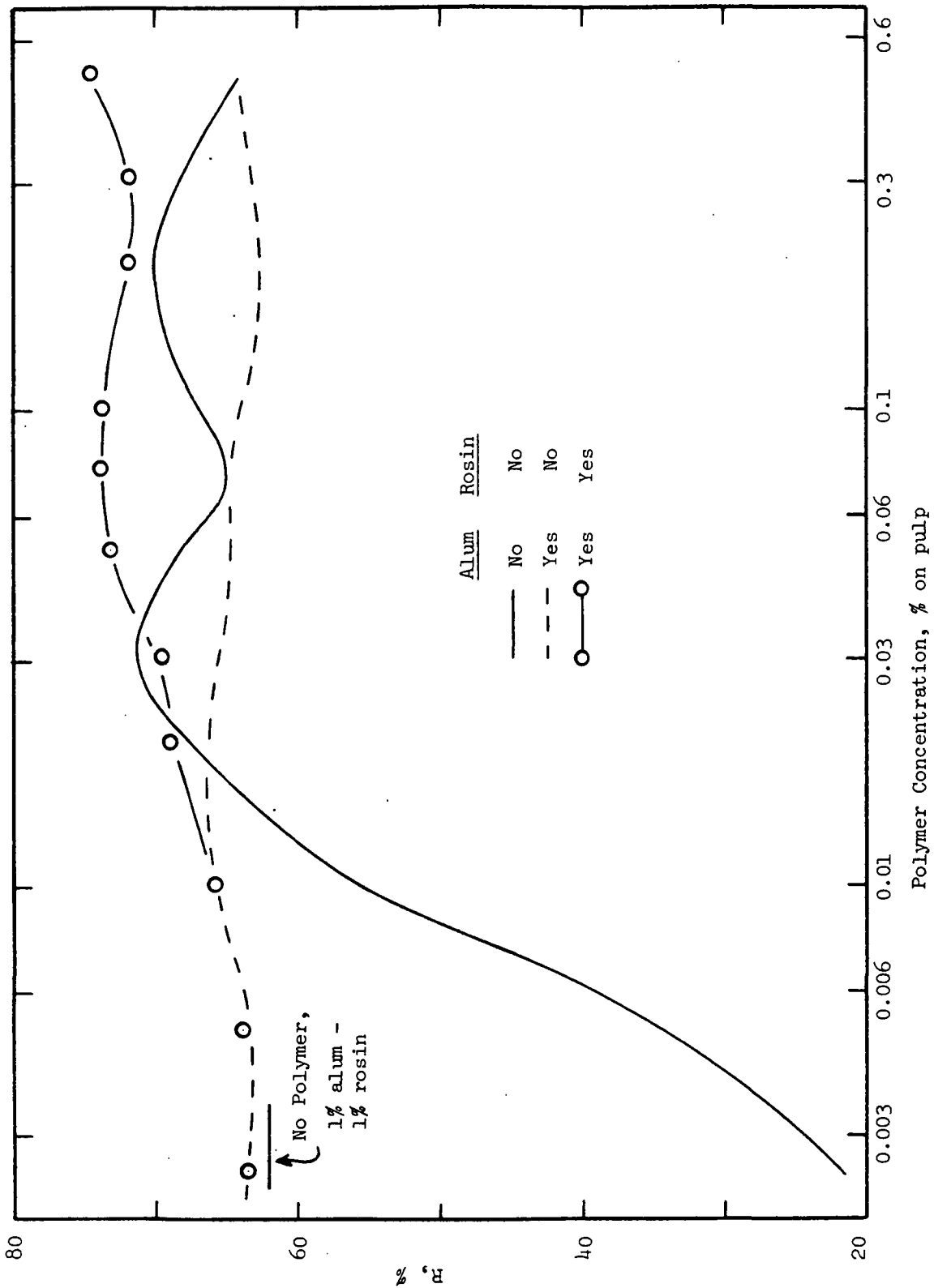


Figure 11. Effect of Rosin/Alum Size on Retention Aid Effectiveness. Polymer: Q100. Contact Time: 40 Sec



alum for sites. The combination rosin/alum/Q100 also produced better retention at moderate polymer dosages than did Q100 alone. The water drop size test (TAPPI Method T492 pm-76) was carried out on representative sheets of the sized paper. No change in the water drop was noted in 10 min for any of the samples, and the test was discontinued at that point. Thus the sizing was good.

### Starches

Starch is probably the largest (by weight) nonmineral, noncellulosic component in many paper mill furnishes. It may be added at the wet end for strength, at the size press for sizing applications, and with the coating as a pigment binder. The starch from the latter two points of application can reenter the papermaking furnish with the broke. The composition of the various starches can range from essentially unmodified to cationically modified to hypochlorite-oxidized containing some anionic character. It is probably safe to say that many of the papermaker's problems with pigment retention originate in the presence of the various starches. As mentioned previously these very hydrophilic materials form excellent protective colloids to disperse the fillers which one would like to retain. A recent review (25) describes many of the problems encountered when using these materials. The present study seeks only to evaluate the interaction of typical starches with cationic poly-electrolytes with respect to their combined effect on filler retention.

Three products encompassing a range of typical kinds of starches were examined. The starches were cooked as described in the Appendix and were added to the furnish before the  $TiO_2$  was mixed in. The results are presented in Fig. 12-14. Two levels of addition, 1 and 2%, of a cationic starch, Cato 8, are compared with the base line curve (no starch) in Fig. 12 with Q100 as the retention aid. It is well known that cationic starch is itself a good pigment retention aid. This is illustrated by the retention levels with the starch but no polymer in the figure.

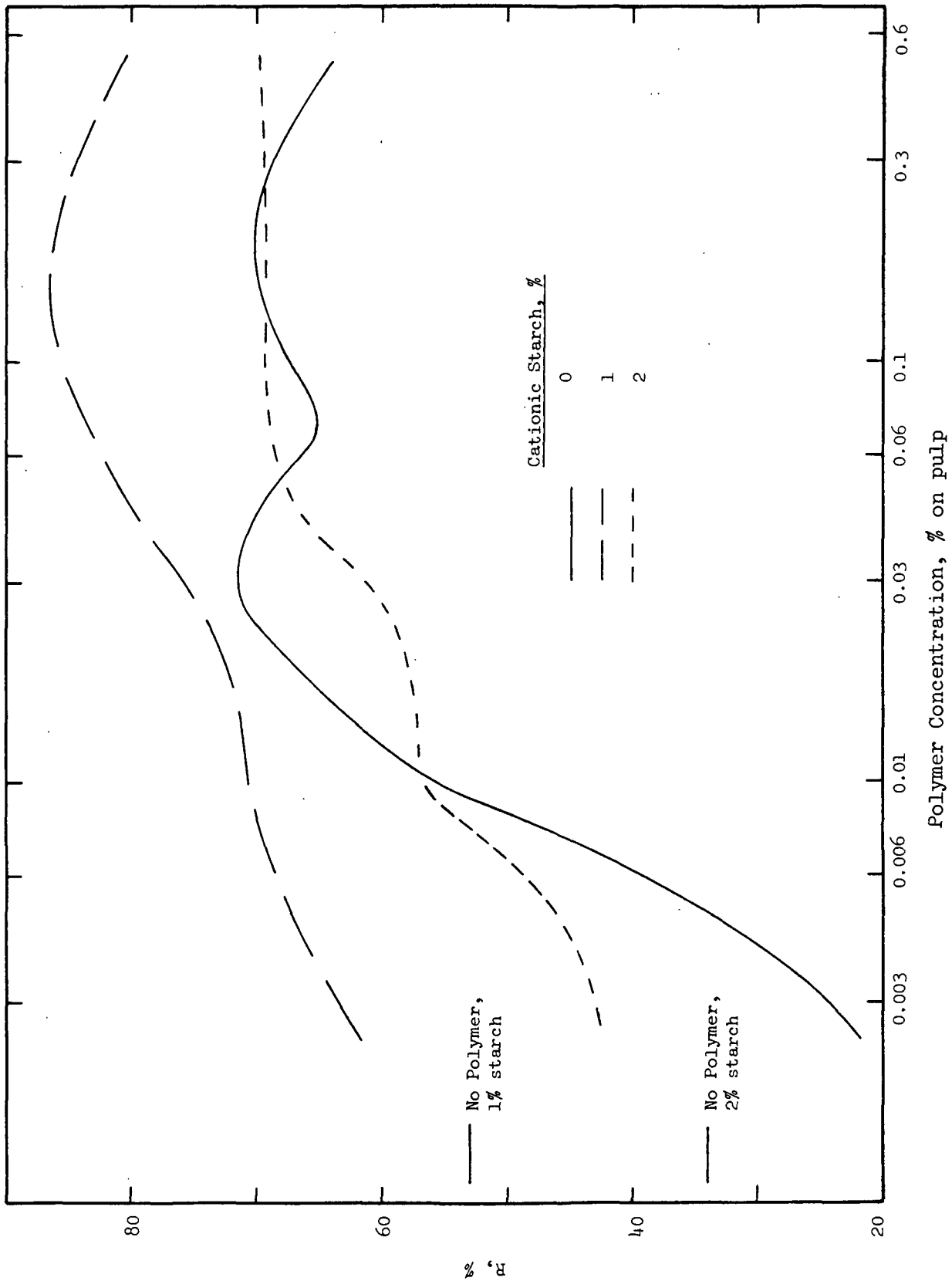


Figure 12. Effect of Cationic Starch on  $TiO_2$  Retention. Polymer: Q100.  
Contact Time: 40 Sec

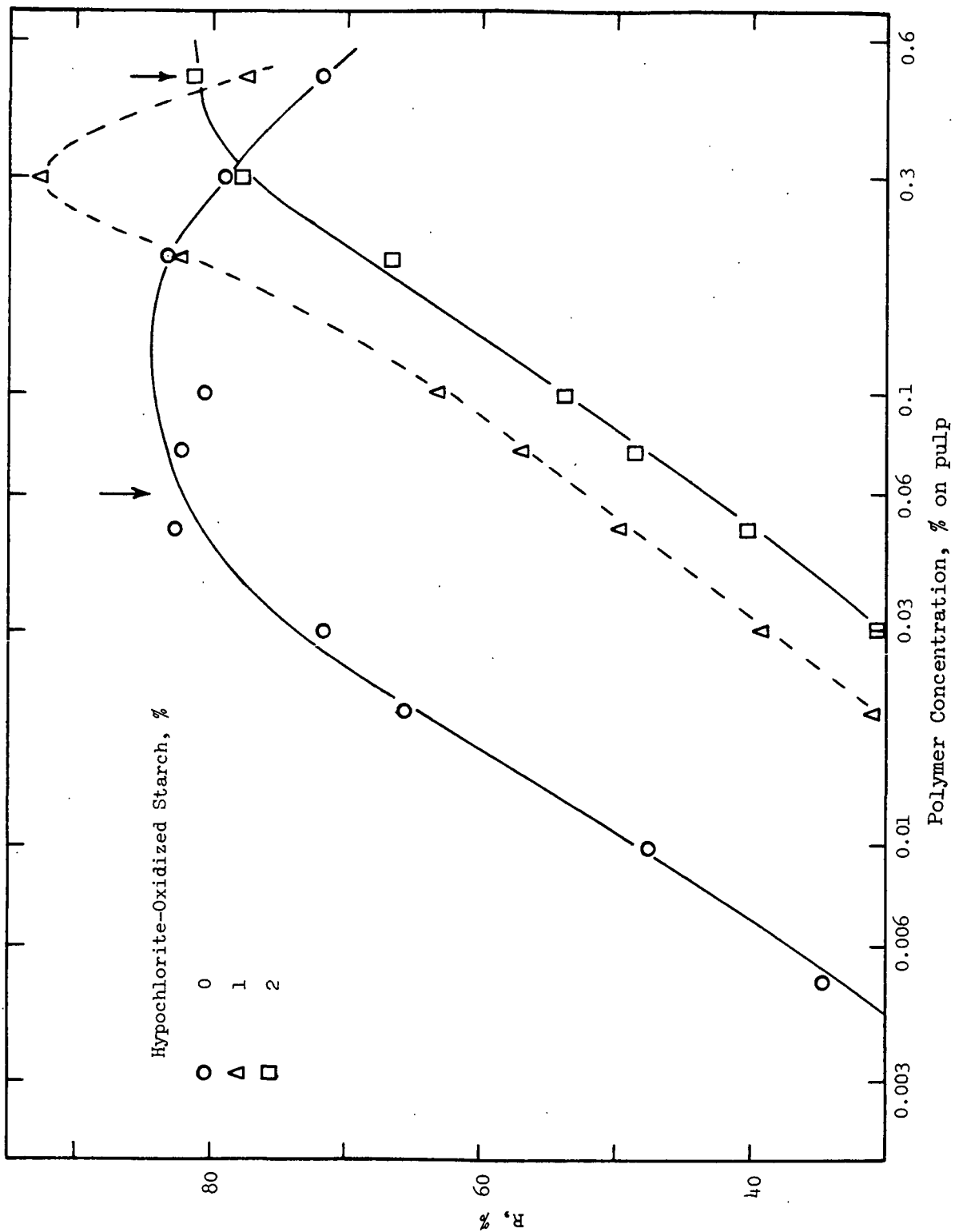


Figure 13. Effect of Hypochlorite-Oxidized Starch on  $TiO_2$  Retention.  
Polymer: Q5. Contact Time: 40 Sec. Arrows Indicate Concentrations at Zero Zeta Potential

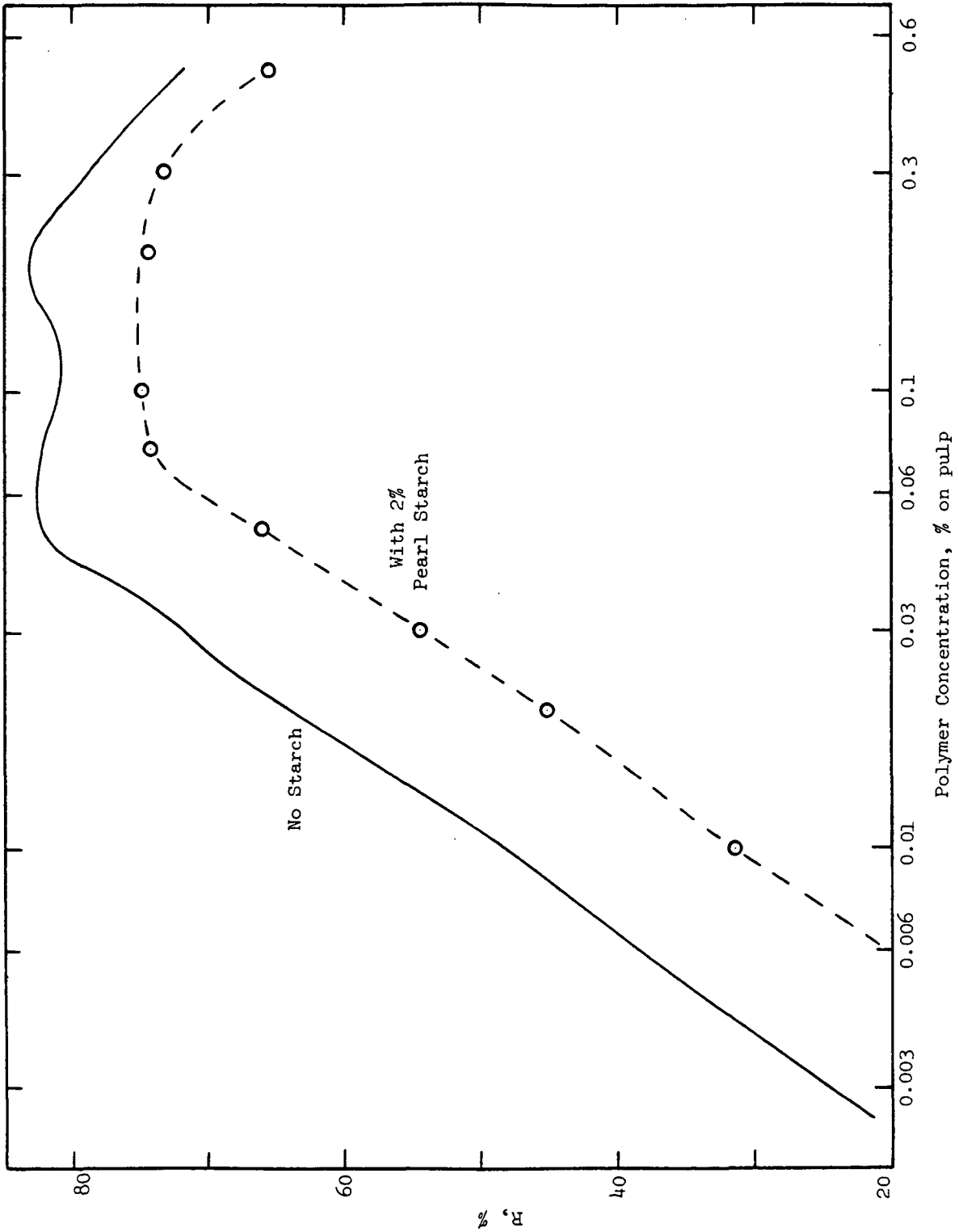


Figure 14. Effect of Unmodified Starch on TiO<sub>2</sub> Retention. Polymer: Q5. Contact Time: 40 Sec

Apparently, 2% Cato 8 represents an overdose for this furnish. At low polymer dosage the interaction of the starch and polymer is additive. As the polymer concentration is increased at the 2% starch level, there is competition for adsorption sites between the two additives. The starch, having been adsorbed first, prevents the polymer from exerting its maximum influence and retention is depressed. At the 1% starch addition level this competition does not exist and the retention aid properties of the two are additive over the whole range of polymer concentrations. Good retention is found over a wide range of dosages.

Hypochlorite-oxidized starch usually enters the furnish with coated broke and has a reputation for drastically reducing the filler retention level. This effect is illustrated in Fig. 13 where levels of 1 and 2% Stayco M have been added to the furnish with Q5 as the retention aid. The drop in retention at typical polymer dosage levels used in mills is over 40% for 2% starch. Two features are of interest. It is apparent that, if the polymer dosage is increased, the retention loss can be recovered. Secondly, the shape of the retention-concentration curves suggests that a horizontal shift will superimpose the three curves. This means that by multiplying the data for the curve with no starch by a factor, the curves at 1 or 2% can be produced. The factors for these two cases are 4.7 and 8.0, respectively. Since hypochlorite-oxidized starch possesses carboxyl groups, the results may only reflect the increased cationic demand of the system. The amount of Q5 necessary to bring the zeta potential of the system to zero should be indicative of this demand and is shown by the arrows in Fig. 13 for the cases of no starch and of 2% starch. The ratio of polymer concentrations at these points is 0.5%/0.06% or 8.3. This confirms the suggestion that the reduced retention upon the addition of Stayco M is merely the result of an increased cationic demand. Exactly parallel results were obtained when Q100 was used as the retention aid with and without 2% Stayco M.

That is, there was a shift of the data along the concentration axis by a factor of 8.0 with the maximum retention at the 2% starch level being approximately the same as that without the starch.

It is of interest that the behavior of Stayco M and the hemicellulose fraction (Fig. 9) both carboxyl-containing polysaccharides, toward Q5 is so different. Perhaps the different levels of addition, 1% and 0.1%, may be responsible. In any case the behavior with Q5 in Fig. 9 is not explicable in terms of cationic demand.

Unmodified corn (pearl) starch does not contain an appreciable number of charged groups and should therefore exert little influence on the cationic demand of the system. Nevertheless, it can lower the filler retention at a given polymer dosage as shown in Fig. 14. Here the furnish was treated with 2% cornstarch and the retention aid Q5. It is possible to approximately superimpose the data (for concentrations below that required for maximum retention) for the system with 2% starch onto the base line furnish by a horizontal shift. However, because the level of retention at the maximum in the two cases is different, and because charge effects should be largely absent, that procedure and the accompanying interpretation is considered incorrect. Instead we propose that there is a general loss in retention of 8-18% depending on the polymer dosage which is a result of the formation of a protective colloid around a certain fraction (at this starch addition level). This fraction is not susceptible to retention via Q5 at moderate concentrations of the latter. At high concentrations (in the vicinity of the maximum) a portion of these sterically stabilized particles is retained.

The same behavior is found when 2% cornstarch is used with Q100 as the retention aid. In this instance the loss in retention at a given polymer dosage ranges from 3 to 16%.

we next examined an unbleached northern softwood kraft (SU), a bleached northern hardwood kraft (HB), and a stone groundwood southern pine (G) pulp. The first two were beaten to a freeness of 300 ml CSF to be of comparable degree of refining to the bleached softwood (SB) kraft (No. 3 whole, 345 ml CSF). The freeness of the groundwood was 42 ml CSF. More details of the composition of these pulps are given in the Appendix. Sheets were prepared on the RMA using  $TiO_2$  and either Q100 or Q5. Contact times of 7.9 and 40 sec were employed to test the development of filler retention with time. For the HB and SU pulps the difference in retention between the two times at a given polymer concentration ranged from 0 to 18% or similar to that found for the SB pulp (see Fig. 1, Progress Report Two). For the groundwood pulp the corresponding changes in retention over that time period was 0 to 6%. Here the much higher fines content increases the collision frequency thereby reducing the time dependence. Only the data at 40 sec will be discussed in this report.

The results for the four pulps are plotted in Fig. 15 and 16 for Q100 and Q5, respectively. The data for the groundwood have been corrected for the ash content of the pulp. The ash contents of the other pulps were negligible. Although the shapes of the curves vary considerably with pulp type and polymer type, the qualitative similarities shown in the figures was unexpected. For example, the maximum retention achieved with Q100 varied from 73 to 84% for the several pulps while that with Q5 varied from 84 to 94%. Again, at a polymer concentration of 0.05% (1 lb/ton) the retention with Q100 varies only from 68 to 79% while that with Q5 varies from 73 to 82%. At lower dosages the differences among the pulps can be substantially greater. For example, at 0.02% (0.4 lb/ton) with Q100 the range is from 51 to 77% and with Q5 from 48 to 65%.

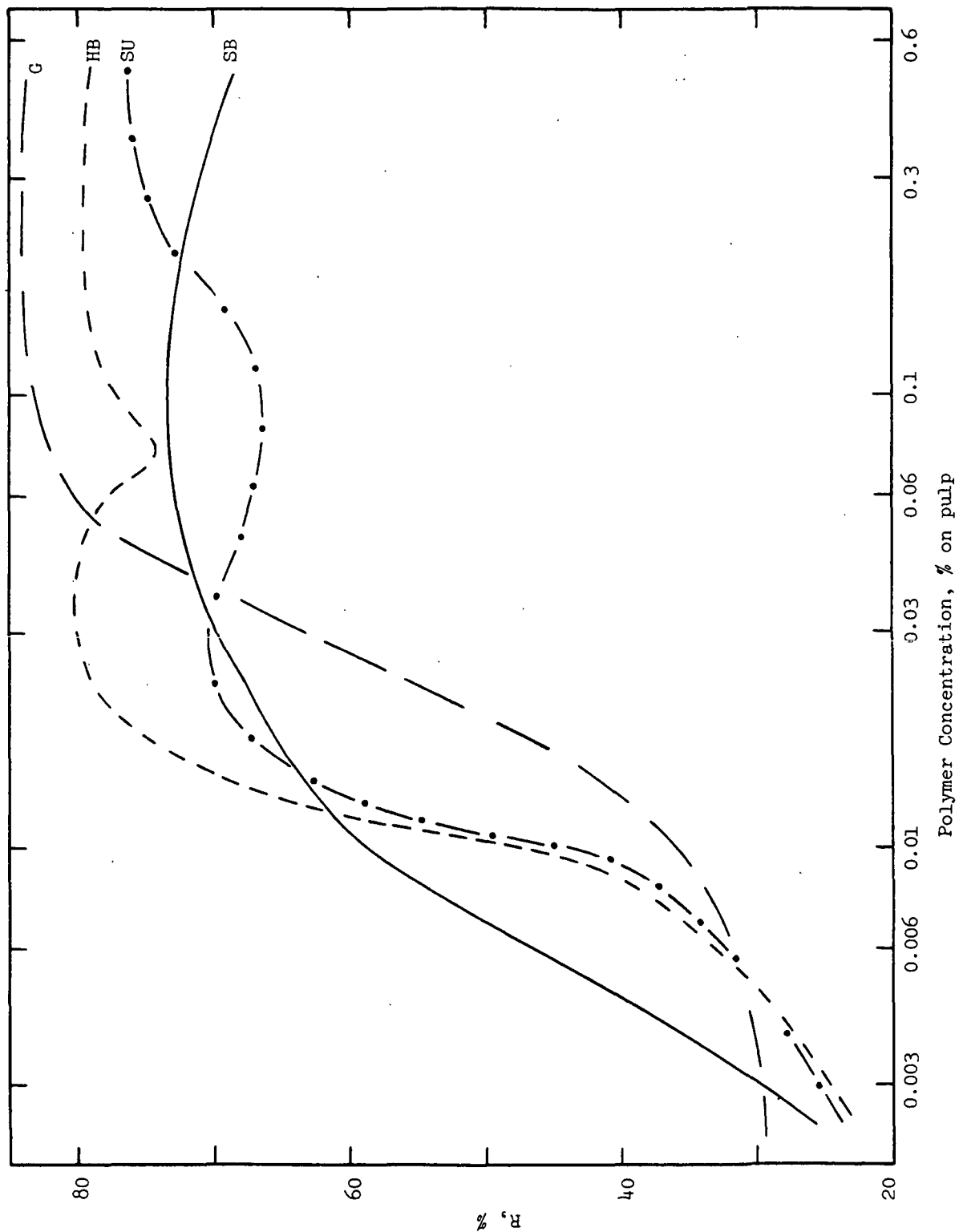


Figure 15. Variation of  $TiO_2$  Retention Behavior with Type of Pulp. See Text for Key to Symbols.  
Polymer: Q100. Contact Time: 40 Sec



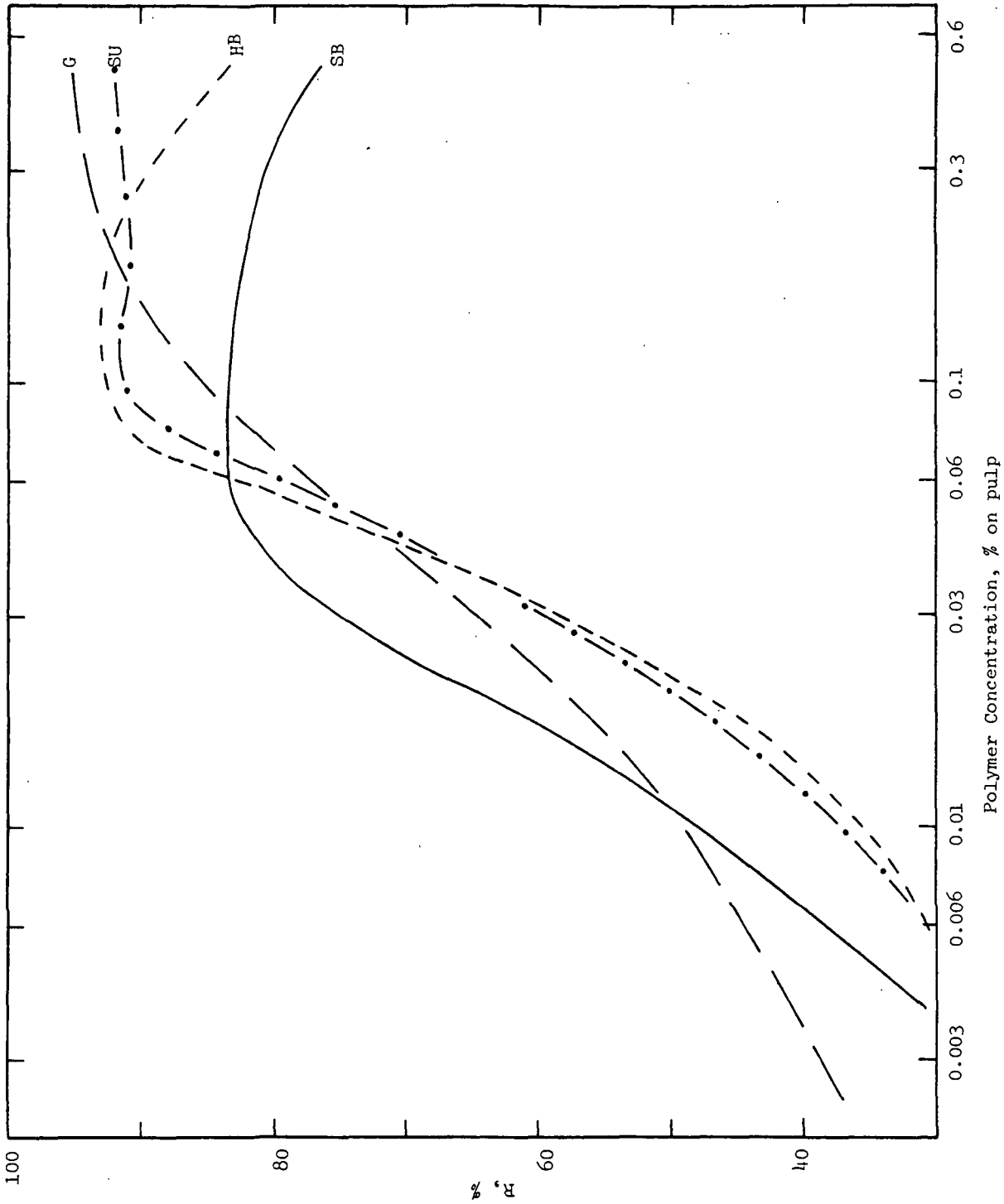


Figure 16. Variation of TiO<sub>2</sub> Retention Behavior with Type of Pulp. See Text for Key to Symbols. Polymer: Q5. Contact Time: 40 Sec

The charge density of the polymers accounts for the somewhat different shapes of curves in Fig. 15 compared with Fig. 16. As discussed previously (5) the region of the maximum corresponding to zero zeta potential is shifted to higher concentrations when Q5 is used, only a single peak is found, and the width of the maximum is narrower. The general conclusion to be drawn from Fig. 15 and 16 is that, with the exception of the groundwood pulp, the use of the high charge density polymer Q100 allows achievement of good filler retention (60-80%) at relatively low dosages. At polymer addition levels of 0.5% (1 lb/ton) or greater, higher values of retention (75-95%) can be attained by using the low charge density Q5. For the groundwood, Q5 provides as good or better retention than Q100 over the entire polymer concentration range. A more detailed analysis of the shapes and relative positions of the individual curves would require additional data such as the quantity and size distribution of fines, the cationic polymer demand, the hemicellulose content, and the fiber carboxyl content. Such characterization is beyond the scope of the present project.

## CORRELATION OF RETENTION AND DRAINAGE

Some exploratory studies using a modification of the RMA to permit a measure of the drainage rate were described in the previous report (5). The conclusion, based on the polymer concentration at the maximum drainage rate compared to that at zero zeta potential (using Q100 with No. 3 whole pulp) was that the drainage aid performed via a bridging mechanism.

The investigation is extended in the present report to include the role of fines and the effect of a rather different pulp, groundwood. As before, rather heavy sheets (in the present instance, final basis weights of 147 g/m<sup>2</sup>) were formed to permit the effect of the drainage aid to be observed. A contact time of 40 sec was used with Q100 as a combination retention/drainage aid.

Because some work (26,27) suggests the mechanism of drainage enhancement to be by coflocculation of the pulp fines onto the fibers, it was of interest to examine the case of few fines. For comparison with the No. 3 whole pulp studied previously (5), No. 3 classified pulp was used. This represents a pulp with considerable refining ( $\underline{S}_w = 13,900 \text{ cm}^2/\text{g}$ ) or fibrillation but with few fines. The retention and drainage results, presented in Fig. 17, confirm our previous work. The major maximum in filler retention occurs near the zero zeta potential indicated here by a vertical arrow. Good retention continues to be found at higher polymer concentrations where the zeta potential is  $\geq 20$  mv. Bridging as the retention mechanism is suggested in this region. The maximum in drainage rate also occurs in this region of high, positive zeta potential. The increase in drainage rate for this essentially fines-free furnish is greater than 50% and provides further evidence for the need for an alternative mechanism of drainage aid action.

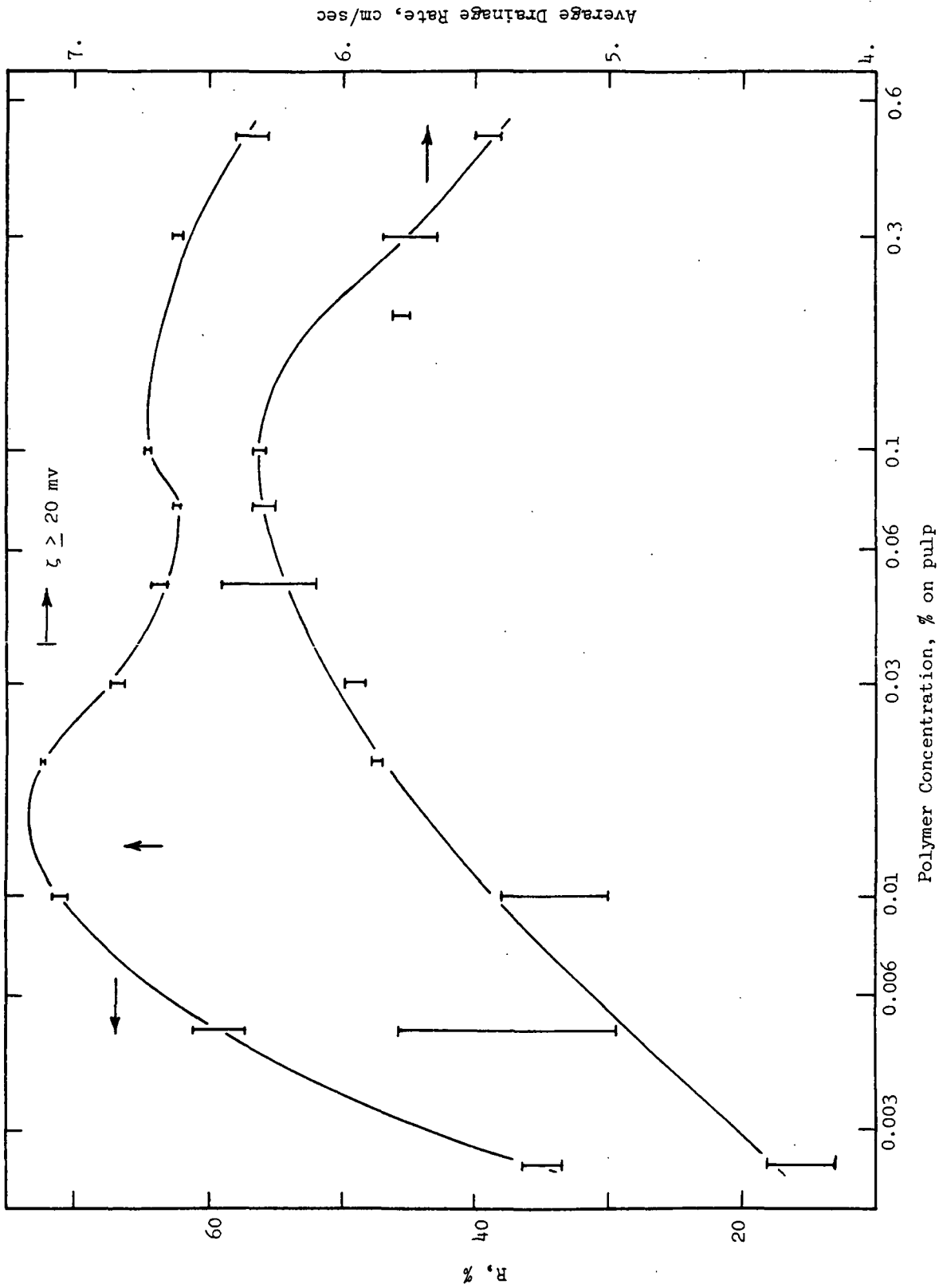


Figure 17. Correlation of Retention and Drainage Behavior of No. 3 Classified Pulp Treated with Q100. Contact Time: 40 Sec. Final Basis Weight: 147 g/m<sup>2</sup>. Vertical Bars Indicate Range of Duplicate Experiments. Vertical Arrow Indicates Concentration at Zero Zeta Potential.

Decreased filtration resistance was shown in earlier work (5) for a classified pulp treated with drainage aids. The change was attributed to a concomitant decrease in the hydrodynamic specific surface area of the fibers. The present results from the modified RMA provide a different experimental technique to corroborate the constant rate filtration results. Moore (28), also, has found drainage enhancement with polymer-treated classified pulps.

Having established the desirability of a large positive zeta potential for maximum drainage enhancement with a bleached softwood kraft pulp (both whole and classified), we must now admit other possibilities. The retention and drainage properties of the groundwood pulp treated with Q100 are presented in Fig. 18. As before the vertical arrow denotes the concentration of polymer required to attain zero zeta potential. The cationic demand for the groundwood is seen to be about a factor of ten greater than that for the No. 3 classified pulp. For this furnish the maximum increase in drainage rate is a factor of 2.5X and occurs near zero zeta potential. At the highest dosage (10 lb/ton) the zeta potential is +23 mv, the  $TiO_2$  retention remains high, but the drainage rate drastically decreases from its maximum value.

The difference in behavior illustrated in Fig. 17 and 18 is difficult to explain at present. To determine whether it is caused by the difference in type of pulp, by the very high level of pulp fines in the case of the groundwood, or by some other factor will require further study. Because of the proximity to zero zeta potential, it seems probable that the mechanism of drainage enhancement with the groundwood furnish is coflocculation of the fines. Microscopic examination of the treated furnish supports this.

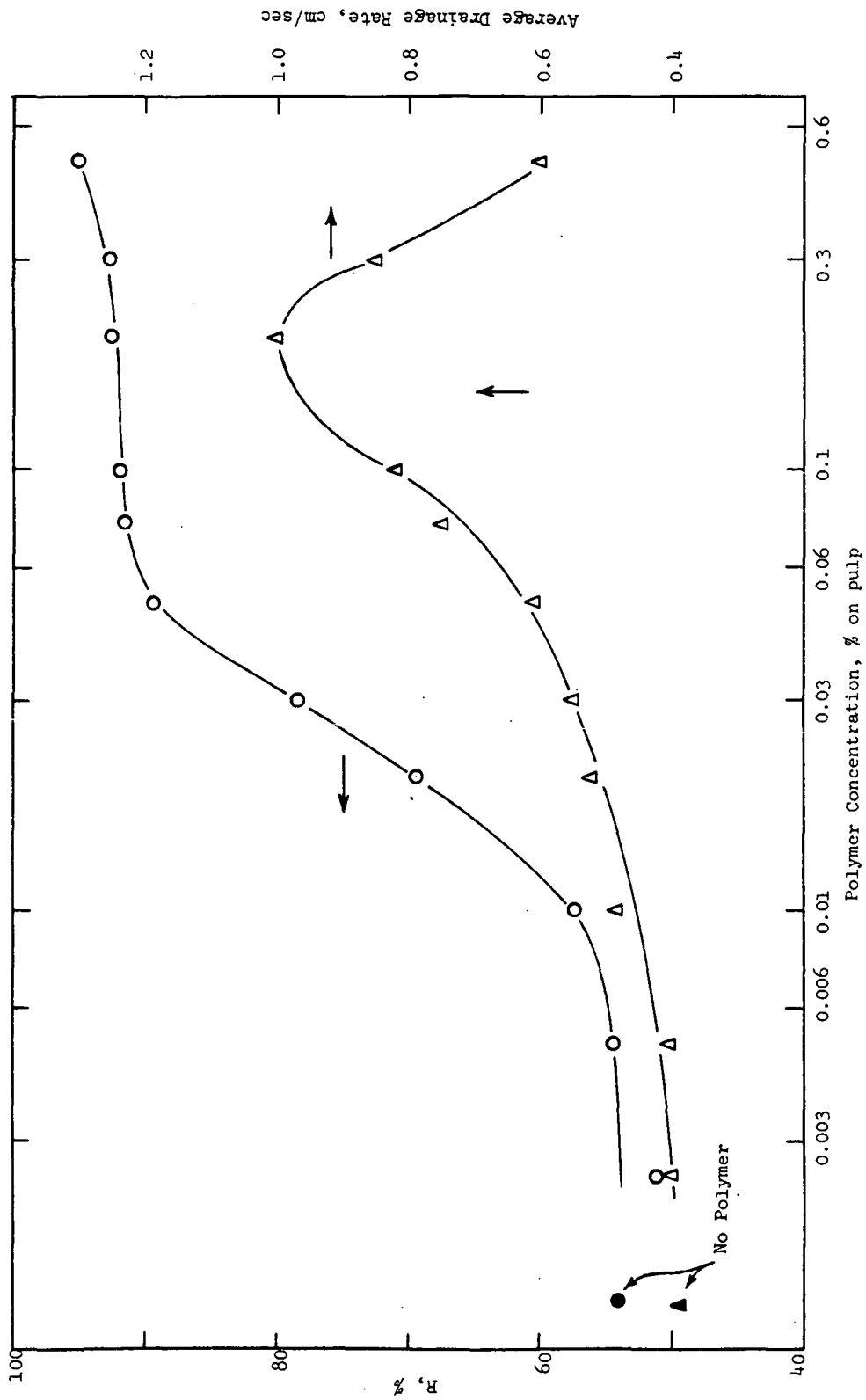


Figure 18. Correlation of Retention and Drainage Behavior of Groundwood Treated with Q100. Contact Time: 40 Sec. Final Basis Weight: 147 g/m<sup>2</sup>. Vertical Arrow Indicates Concentration at Zero Zeta Potential

On the basis of the results for the No. 3 whole pulp (Fig. 21, Progress Report Two) and the groundwood two generalizations may be tentatively advanced. Acceptable levels of retention can be achieved although the zeta potential of the furnish is negative ( $\sim -10$  mv). Somewhat larger dosages of polymer are required to optimize the drainage rate. At these dosages the retention will still be near maximum. The decision, whether or not to maximize the drainage, must involve an analysis of the economics (costs and benefits throughout the papermaking system) as well as the effect of the drainage aid on the strength and formation of the paper and on the optical efficiency of the pigment.

ADDITIONAL INFORMATION

The reader can appreciate that the quantity of experimental data generated in this project on filler retention as a function of polymer type, polymer concentration, contact time, pigment type and pulp type is large. The important findings have been presented for the most part in the form of graphs in this and the previous reports. Rather than increase the bulk of this report unnecessarily, the data have been separately tabulated. Copies of these tables can be obtained from the authors upon request.



## FUTURE WORK

Two main topics will be investigated during the balance of the time period of this project (through April 30, 1977). The first of these concerns the effect of the feed concentration of the polymer retention aid at the point of introduction to the stock. The time required for polymer adsorption was deduced to be very short in the first part of the present report. The necessity of rapid, even distribution of the polymer to the flowing stock is obvious. The polymer feed concentration will be varied (at constant dosage) and the effect on retention and the optical efficiency will be investigated.

The second topic, which will partly encompass the first, will be concerned with methods to maximize the pigment optical efficiency. The effects of polymer feed concentration, polymer dosage, location and method of polymer introduction, and order of addition of the various furnish components will be among the parameters studied. The objective here is to determine those conditions which will allow the papermaker to obtain the maximum opacity from his pigment.

#### ACKNOWLEDGMENTS

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## LITERATURE CITED

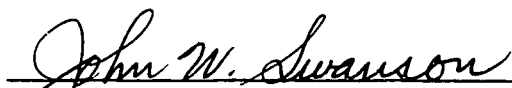
1. Lindstrom, T., Soremark, C., Heinegard, C., and Martin-Lof, S., Tappi 57(12):94(1974).
2. Ruehrwein, R. A., and Ward, D. W., Soil Sci. 73:485(1952).
3. Gregory, J., Trans. Faraday Soc. 65:2260(1969).
4. Gregory, J., J. Colloid Interface Sci. 42:448(1973).
5. Stratton, R. A. and Swanson, J. W. A fundamental study of the mechanisms of action of polymers as retention and drainage aids. Progress Report Two, Project 3275, Appleton, WI, The Institute of Paper Chemistry, October 6, 1976.
6. Lindquist, G. M. and Stratton, R. A., J. Colloid Interface Sci. 55:45(1976).
7. Osmond, D. W. J., Vincent, B., and Waite, F. A., Colloid Polymer Sci. 253:676(1975).
8. Willets, W. R., Paper Trade J. 102(3):36(1936).
9. Brill, H. C., and Hecklau, F. L., Tappi 43(4):229A(1960).
10. Stratton, R. A. and Swanson, J. W. A fundamental study of the mechanisms of action of polymers as retention and drainage aids. Progress Report One, Project 3276, Appleton, WI, The Institute of Paper Chemistry, March 10, 1976.
11. Gregory, J. and Sheiham, I., Brit. Polymer J. 6:47(1974).
12. Britt, K. W., Tappi 56(3):83(1973).
13. Britt, K. W., Tappi 56(10):46(1973).
14. Unbehend, J. E., Tappi 59(10):74(1976).
15. Arvela, P., Swanson, J. W., and Stratton, R. A., Tappi 58(11):86(1975).
16. Goossens, J. W. S. and Luner, P., Tappi 59(2):89(1976).
17. Williams, D. G., Baum, G. A., and Swanson, J. W. Improving retention of particulate matter when employing recycled white water. Progress Report One, Project 3245, Appleton, WI, The Institute of Paper Chemistry, August 25, 1975.
18. Guender, W., and Auhorn, W., Paper, World Research and Development Number:20 (1975).
19. Huettner, D. J., Hoffman, G. R., and Swanson, J. W. Improving retention of particulate matter when employing recycled white water. Progress Report Three, Project 3245, Appleton, WI, The Institute of Paper Chemistry, April, 1977.

20. Lowe, K. E., Pulp & Paper, December, 1975:104.
21. Frankle, W. E., and Sheridan, J. L. Tappi 59(2):84(1976).
22. Moore, E. E., Tappi 58(1):99(1975).
23. Arnson, T. R., Unpublished work, The Institute of Paper Chemistry, 1976.
24. Arnson, T. R., Thesis in progress, The Institute of Paper Chemistry.
25. Stoutjesdijk, P. G. and Smit, G., Paper, World Research and Development Number: 42(1975).
26. Ellis, W. H., and Foster, W. A., Paper Trade J. 152(23):34(1968).
27. Linke, W. F., Tappi 51(11):59A(1968).
28. Moore, E. E., Tappi 58(1):99(1975).

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## APPENDIX

## PREPARATION AND DESCRIPTION OF MATERIALS

## CLAY

A 50% solids dispersion of WPSD grade Georgia Kaolin Clay, containing dispersant, was prepared by adding 200 grams of dry clay (as received) to 200 ml of distilled water in a Waring Blendor and then stirring at high speed for 2 minutes. The dispersed clay was stored on a slowly rotating rack for use in the future. The clay was incorporated in the furnish by adding an amount to the 1/2% consistency pulp stock to constitute a 10% addition level based on o.d. pulp fiber. The pH was adjusted to 5.0 with H<sub>2</sub>SO<sub>4</sub> and the mixture was stirred for about 15 minutes before beginning a run on the RMA to form handsheets.

The KWW filler clay (Engelhard Minerals & Chemical Corporation) was dispersed at 10% solids by adding it to distilled water containing tetra sodium pyrophosphate dispersant (0.3% based on clay solids) in a micro-Waring Blendor. The blendor was operated at a low speed during clay addition to the water and, after all the clay was added, at high speed for 30 seconds to disperse the clay. After dispersion the clay was immediately added to the 1/2% consistency pulp stock, and the mixture was stirred for 15 minutes at an adjusted pH of 5.0 as mentioned above.

Values of retention from ashing were corrected for water loss during ashing by division by the ratio (0.864) of the ash weight to the o.d. weight of the clay (17).

#### HARD WATER

Artificial hard water was prepared by dissolving the chemicals listed below in 25 liters of distilled water:

2.295 grams of  $\text{Ca SO}_4 \cdot 2 \text{H}_2\text{O}$

7.106 grams of  $\text{Ca Cl}_2$

3.093 grams of  $\text{Mg SO}_4$

1.725 grams of  $\text{Na H CO}_3$

9.595 grams of  $\text{Na}_2\text{SO}_4$

This provided 435 ppm hardness as  $\text{Ca CO}_3$  at a 7.3 pH. The hard water was used in the disintegration and dilution of the pulp and also for polymer dilution.

#### HEMICELLULOSE

A 50 g batch of unbeaten bleached kraft northern softwood pulp was extracted with successive volumes of 667 ml of 1, 8, and 16% concentrations of NaOH for periods of two hours each under vacuum. After the two hour extraction time the pulp was drained on a Buchner funnel, washed twice with 167 ml NaOH (same concentration as used for extraction) and once with distilled water. The filtrate and washings from the 16% extraction were combined, adjusted to pH 6 with glacial acetic acid, and then filtered through sintered glass and added to 2.67 liters of 95% ethanol. Floccs formed and were allowed to settle overnight. The supernatant was then decanted and the remaining floccs in the alcohol were collected by means of centrifugation. The floccs were washed twice with ethanol, slurried in 50 ml distilled water, and evacuated in a rotary evaporator to remove the ethanol. The water was removed by freeze drying.

The 16% NaOH extraction was analyzed for sugars and the results are listed in Table II.

TABLE II  
SUGAR ANALYSIS OF HEMICELLULOSE  
(16% NaOH Extraction)

Sugar	Extracts, %
Araban	0.02
Xylan	4.6
Mannan	19.3
Galactan	0.5
Glucan	5.6

Dissolution of the hemicellulose powder (16% NaOH extraction) was accomplished by adding 0.05 g to 20 ml of distilled water, with agitation, and then adding 9 ml of 20% NaOH. After the hemicellulose dissolved, the pH was adjusted to 7.0 with 20% H<sub>2</sub>SO<sub>4</sub>.

The hemicellulose solution was added (0.1% add-on level based on o.d. pulp) and mixed in for 10 minutes after the TiO<sub>2</sub> had been mixed with the 1/2% consistency pulp for 15 minutes. Adjustment of the pH to 5.0 with H<sub>2</sub>SO<sub>4</sub> was made prior to beginning sheet preparations on the RMA.

#### ROSIN SIZE

A solution of fortified rosin size, PEXOL 277 (77% solids) (Hercules, Inc.) was prepared by dissolving the paste in 50°C distilled water, with stirring, at approximately 15% solids. The solution was filtered through Whatman No. 1 filter paper and the solids determined. Prior to being used in handsheets, the rosin was subsequently diluted to 5% solids with distilled water. A 1.0% addition

level of rosin size was added to the 1/2% consistency pulp slurry after the  $TiO_2$  had been mixed in for 15 minutes and was followed by a 1.0% addition level of alum. Both the rosin and alum addition levels were based on pulp solids and, each was mixed in for 5 minutes. The pH was 4.7 after alum addition and was not further adjusted prior to making handsheets.

#### STARCHES

The following three starches were incorporated in handsheet furnishes for retention studies:

Name	Type	Manufacturer
Cato 8	Cationic cornstarch	National Starch and Chemical Corporation
Stayco M	Hypochlorite oxidized low viscosity cornstarch	Staley Manufacturing Company
Globe 3001	Unmodified pearl cornstarch	Corn Products Sales Company

For use in handsheet preparation each starch was cooked separately at 5% solids in distilled water at 90-95°C for 30 minutes over steam. Immediately following cooking the unmodified starch was diluted to 2% solids with hot distilled water, whereas the cationic or hypochlorite oxidized starch was diluted to 1% solids. After dilution the starch was cooled to 25°C prior to addition to the pulp. The starch was added to the 1/2% consistency pulp and mixed in for 10 minutes prior to mixing in the  $TiO_2$  and adjusting pH to 5.0 with  $H_2SO_4$ . Unmodified starch was incorporated at a 2% addition level whereas the cationic or hypochlorite-oxidized starch was added at 1 and 2% level based on o.d. pulp fiber.



OTHER PULPS

There were three other pulps used for experimental work, and their descriptions are listed below:

Groundwood, Champion International, Southern Pine Stone Groundwood

Softwood unbleached kraft, St. Regis Paper Co. 100% softwood unbleached kraft, medium cook. Principle species: Douglas-fir, spruce and/or hemlock, traces of pine

Hardwood bleached kraft, Escanaba bleached hardwood "Red Buck," Mead pulp sales - 95% hardwood bleached kraft. Principle species: Populus group, some maple, basswood and birch, traces oak, beech and chestnut - 4% softwood bleached kraft. Principle species: southern and jack pine, some white pine, traces spruce and hemlock

The softwood unbleached kraft and hardwood bleached kraft pulps were individually refined to a 300 cc Canadian standard freeness in deionized water with a 1 lb Valley beater and then dewatered to 25-30% solids.

All of the above pulps were stored at 5°C with 1% of formaldehyde added for preservative.

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