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THE INTERRELATIONSHIP OF
FIBER LENGTH TO TITANIUM
DIOXIDE PIGMENT RETENTION

by
Robert A. Hansen

A Thesis Submitted
in Partial Fulfillment of
the Course Requirements for
the Bachelor of Science Degree

Western Michigan University
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ABSTRACT

A literature review is presented that reviews the various considerations of retention in papermaking. The definition of retention and the three methods of retention, (sieving, entrapment, and coflocculation), are reviewed. Coagulation and flocculation are respectively discussed. Zeta potential and the various methods with which it is measured are reviewed, as well as various factors that influence zeta potential. The role of fines in the retention of wet end additives in the papermaking process is also discussed.

An experiment is designed to evaluate the effect of fiber length on titanium dioxide pigment retention. The experiment involves the determination of an optimum level of addition of a cationic retention aid in order to achieve maximum retention of titanium dioxide pigment in a papermaking furnish. A Laser-Zee microelectrophoresis meter was used to determine this point of optimum flocculation.

A 50% hardwood- 50% softwood furnish was prepared and beaten to a CS freeness of 500. This pulp was fractionated with a Clark Fiber Classifier into four different distributions. Each fiber fraction was placed in a Dynamic Drainage Jar at 0.5% consistency along with 20% by weight of fiber TiO_2 . Three different levels of retention aid addition and three different levels of shear were used with each fiber length. 100 ml samples were taken at each level of shear and each level of addition. These samples were filtered and ashed in order to determine retention of the TiO_2 .

The results showed a significant improvement in retention at levels of retention aid 100 and 200 times the calculated optimum addition level of 0.001 lb./ton. Optimum retention was obtained at the lowest level of shear for each fiber length. Shorter fibers appeared to provide better retention than longer fibers, regardless of shear rate and retention aid level.

INTRODUCTION

Retention of fines and fillers on the wet end of a Fourdrinier paper machine has long been a concern to the paper maker. The effect of fines content on drainage rate and strength properties is well documented. However, the influence of fiber length on retention is not as well defined. This paper will attempt to examine the effect of fiber length on titanium dioxide retention, and whether or not shear rate has any effect on this relationship.

RETENTION

Retention may be defined fundamentally as the holding of all additives and fines in the moving web of paper. Increased retention can mean better quality paper, lower operating costs, and reduce the consumption of raw materials. It can also result in reduced BOD loads in the mill effluent.

There are three methods of retention. Many authors (1, 2, 3, 4,) have discussed the significance of these methods. These methods are: 1) sieving, the process of removing particles larger than the pore openings during sheet formation; 2) entrapment, the physical collection of particles on the fiber surface, in the fibril structure, or in the fibril lumens; and 3) coflocculation, the interaction of the interfacial forces of the particles which control ordinary colloidal flocculation. Coflocculation can occur in either one of two mechanisms: 1) coagulation, the collapse or compression of the electric double layers of the particles; or 2) flocculation. Coflocculation has been found to be the dominant mechanism for retaining pigment fillers and pulp fines (5).

THEORETICAL CONSIDERATIONS

Coagulation and Flocculation

Coagulation of colloidal suspensions is a phenomena dictated by free surface energies. A colloidal suspension is characterized by large free surface energies. If an aggregated state of colloids possesses a lower total free energy than the suspended state, the colloidal dispersion should coagulate.

Systems may resist this coagulation. The particles may be held apart by one or more of the following phenomena: 1) electrostatic repulsion barriers between the double layers of two similarly charged particles; 2) steric stabilization; and 3) hydration of the particle surface (physical hindrance).

In a study done by Black, Birkner, and Morgan (6), it was found that the adsorbed layer of water on a hydrated surface is only a few molecules thick. This would imply that minimizing the distance of closest approach would only be of concern when short-range particle interactions are to be considered.

In order for a system of particles to exist in a dispersed state, the electrostatic charges present on the particles will exert a repulsion between the particles that is large compared to the free energy of the particles. Electrostatic charges may develop on solid surfaces in contact with a liquid in essentially three ways: 1) direct ionization of the substance; 2) preferential adsorption of a particular type of ion; or 3) isomorphous lattice substitution (7). The acquisition of a charge or charges produces a barrier of electrical charge around the particle referred to as the electrical double layer.

Sikora produced a study of polyelectrolyte effects on colloidal dispersions (7). In this study he discussed two different methods of flocculation of colloidal particles with polyelectrolytes:

1) if the polyelectrolyte has only a few charges, bridge-type flocs will form (initially proposed by LaMer and Healy (4)); and 2) if the polyelectrolyte has many charges on it, patch-type flocs will form. Bridge type flocs involve the few charges on the chain. If this

chain contacts the negative fiber or filler particle in solution, very few of the segments of its chain will attach to the fiber or particle, leaving the rest of the chain dangling out in solution. When this chain comes close enough to a chain from another particle, the chains will bridge themselves together and floc will form. Flocs formed with these polymer bridges have a fishnet form and may be easily deformed (i.e., high shear rates).

A different phenomena occurs when a polyelectrolyte filament carries a great deal of charge. Here we have a negatively charged particle in solution and a polyelectrolyte chain with many positive charges on it. Because of all the opposite charges, the polyelectrolyte is strongly adsorbed and in a configuration resembling a flat pancake. Attractions of other particles to this pancake-like patch occurs in much the same fashion as the attraction of opposite poles of two magnets. Patch-type flocs are very dense and do not deform very easily. This may suggest that shear rates developed in the wet-end of the paper machine are high enough to destroy some floc and not others.

Zeta Potential

One model of this electrical double layer which has gained wide acceptance is that proposed by Gouey-Chapman-Stern (Figure 1). This model consists of an inner layer of hydrated ions next to the particle (Stern layer) and a diffuse layer of counter-ions (Gouey-Chapman layer). The ions in the Stern layer are very strongly adsorbed and are mobile. These ions are distributed according to the sum of their characteristic thermal energies and their electrostatic attractions to the surface. The further away from the

FIGURE 4a

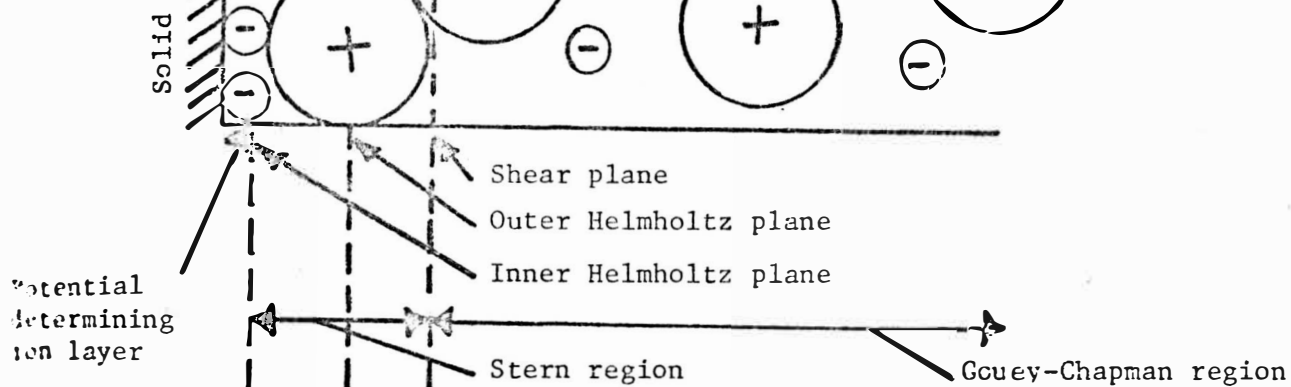


FIGURE 4b

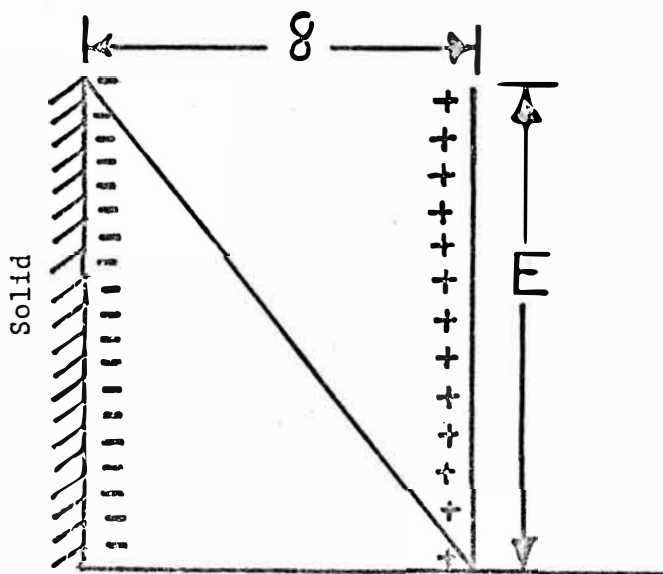
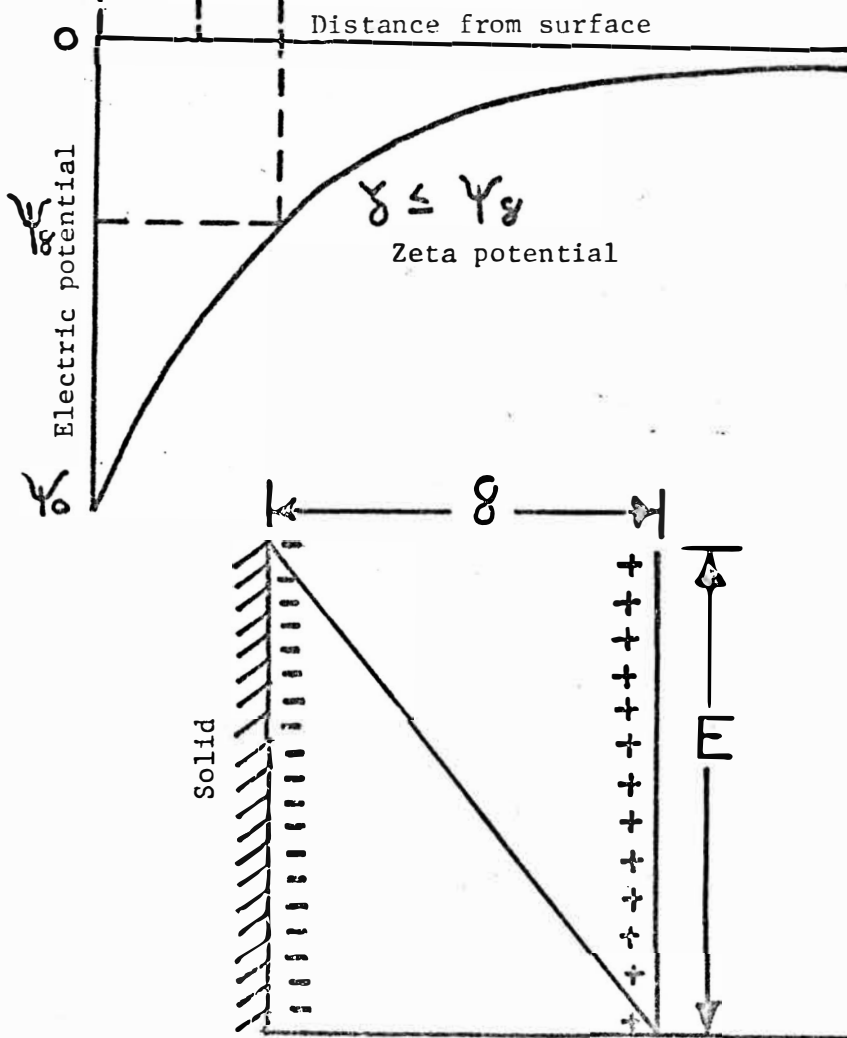


FIGURE 1

particle surface, the lower the electrical potential. This potential decreases exponentially with distance. The outer boundary of the diffuse layer exists at the point in which ionic electroneutrality is re-established. The potential at the hydrodynamic plane of shear is commonly referred to as the zeta potential, ζ . Its value is equal to or slightly less than the potential at the Stern layer. Zeta potential () is calculated by the formula: $\zeta = \frac{4ed}{D}$ in which e = electrical charge associated with the particle, d = thickness of the double layer, and D = dielectric constant of the medium.

The thickness of the electrical double layer may be approximated as the reciprocal of the Debye-Huckel parameter, κ .

$\kappa = eZ \sqrt{(8\pi n)/EKT}$ where e = elementary charge, Z = valence of the ions, n = solution ion concentration (ions/ml), E = dielectric constant of the bulk solution (farads/cm), K = Boltzman's constant, and T = absolute temperature.

If the double layer thickness, the spherical radius of the particles, and the ζ potential are known, it is possible to estimate the repulsive potential between interacting particles, providing the real system can be approximated by any of the interactions, sphere-sphere, sphere-plate, or plate-plate, as proposed by Hogg, Healy, and Fuerstenan (8).

To calculate a value for the attractive potential energy, Vincent's (9) equations may be used, which have the following form: $-12V_A = \sum_{ij} f^n(A_i)H_j$ where $f^n(A_i)H_j$ is a function of the Hamaker constants A_i , of the various materials, and of the geometry of the system, H_j . By describing H for use at short and long distances

of separation, one could successfully calculate V_A for large and small distances of separation.

Once a potential energy diagram of V_T versus H_0 has been constructed, the stability of the system can be defined in terms of a stability ratio, W , which is given by $W = 2 \int_1^{\infty} e^{(V_T/KT)} \frac{ds}{s^2}$ where $s = r/a$, r being the minimum distance of separation and a being the radius of the particle.

Theoretically, the zeta potential must be reduced to about -10 mv. before the repulsive force is balanced by an attractive force first defined by Van der Waal (10). Ideally, a zeta potential of 0 mv. is the point of ideal flocculation. This point is referred to as the isoelectric point, which is the pH at which the zeta potential is zero.

METHODS OF DETERMINING ZETA POTENTIAL

Four main procedures for the measurement of zeta potential are currently available: 1) electrophoresis; 2) sedimentation potential; 3) streaming current; and 4) electroosmosis (11). Electrophoresis involves placing an electrical potential across a liquid suspension. This electrical potential causes the particles to move toward the poles carrying a charge opposite to that of the particle itself. Britt and Unbehend (12) examined a method which is included in this class known as mass transport. This method permits the use of a wide range of particle sizes in the measurement, and is also a convenient method to determine the influence of carboxyl content of pulp on zeta potential.

Sedimentation potential involves the development of a potential difference when charged particles are allowed to settle from a dispersion.

The streaming current method involves development of a current when a liquid is caused to move past a charged surface. This method utilizes a preformed fiber pad. Inherent difficulties with this technique involve the formation of a uniform pad and the inability to analyze dynamic systems since the surface potentials continually change under the influence of hydrodynamic shear (13, 14).

By applying an electrical potential difference, liquid can be caused to move through a capillary tube. This is the basis for electroosmosis (15).

The most popular methods used are the streaming current method and microelectrophoresis. Microelectrophoresis involves the observation of the motion of small, nonsettling particles in an electric field. The Lazer-Zee meter involves this type of measurement and will be used in the experimental work.

ADSORPTION

Recent works by Fumihiko Onabe (16, 17) discuss the mechanism of the adsorption of cationic polymer on cellulose fiber. Conclusions made are as follows: 1) electrostatic adsorption of cationic polyelectrolytes is stoichiometric with the carboxyl concentration on the fiber surface; 2) high molecular weight cationic polyelectrolyte is more readily adsorbed than low; 3) a monolayer of cationic polyelectrolyte is ultimately formed on cotton linters and dissolving pulp, respectively, as a result of electrostatic and

Van der Waals' forces; and 4) in the process of forming a monolayer, cationic demand plateaus are formed, which can serve as useful measures of electrostatic charge neutralization. Onabe also proposes a dual mechanism for the interaction of cationic polyelectrolytes with cellulosic fibers in which the primary adsorption occurs to the point of charge neutrality, probably due to an ion exchange mechanism, and the secondary adsorption takes place as a result of Van der Waals' force on hydrogen binding.

Anderson and Penniman (18) performed a study concerning optimum control for the paper mill wet end. Two significant findings of this study were: 1) the optimum zeta potential of -3 mv. to +5 mv. should replace the commonly accepted -5 mv. to +5 mv. range; and 2) the length of the plateau on the graph of zeta potential versus pH is a measure of the cationic demand, or the adsorption-neutralization characteristics of a particular pulp.

FACTORS CAPABLE OF INFLUENCING ZETA POTENTIAL

In paper mill wet end chemistry, chemicals are often added to adjust the zeta potential close to zero in order to obtain maximum efficiency. This zero point is referred to as the isoelectric point. The isoelectric point is, by definition, the pH at which the zeta potential is zero. The isoelectric point of several fillers is shown in Table 1 (8).

Iso-electric Points of Fillers Used

	i.e., p/pH
Anatase A-HR	4.0
A-DM	3.8
Rutile R-CR	6.2
R-HD6	6.8
Hydral	9.0
Silica	2.0
Stannic Oxide	5.8

Table 1

The isoelectric point of cellulose fiber is at a pH of approximately 2.5. Since a liquid system with a pH of 2.5 would react with the papermaking machinery and rapidly corrode it, other means of pH adjustment are used in the papermaking process to bring the zeta potential close to zero. The AL^{+3} ion which results from the use of alum, and various other cationic polyelectrolytes, are very effective in moving the zeta potential of the negatively charged particles toward zero (10).

The water used in the furnish also has an effect on the zeta potential. Figure 2 plots zeta potential of titanium dioxide (anatase) versus pH for tap water and white water (19).

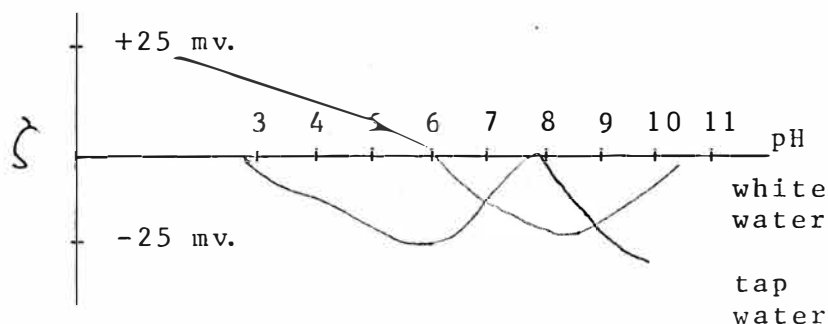


Figure 2

It will be noticed that in order to obtain a zeta potential near zero, one does not need the same pH. It is therefore believed that, depending on the nature of the water, one will not have the same zeta potentials for the same pH.

The theory behind the effect of the addition of electrolytes is that the diffuse layer is compressed and subsequent shifting of counter-ions from the diffuse layer to the Stern layer occurs. This increased concentration of ions in the Stern layer reduces the Stern potential and thus the height of the energy barrier. The attractive forces between particles may then operate to aggregate the system.

FINES

Most papermaking furnishes contain a large amount of fine particles besides the long fibers. These fines play an important role in drainage and retention, as well as in strength development and other sheet properties.

There exist many different opinions and contradictory statements on the effects of fines. One major factor to this confusion is the vague definition of what fines are. Jaycock (8) considered all soluble or colloid dimensioned material in his furnish as fines. Hinton and Quinn (20) took the part of the furnish that passed through a 60-mesh wire as fines. Janes and Reif (21) defined fines as "fraction of particle size which passes a fourdrier wire and consists of a complex mixture of fragments of primary and secondary fiber walls, fibril bundles, fibrils, colloidal matter, short fiber pieces, ray cells, parenchyma cells, and vessel

segments and fragments (in the case of hardwoods)". Marton (22) calls fines the part of the furnish that passes through a 200 mesh screen.

Because of their small particle size, fines have a much larger surface area than coarse fiber components. Pulp fines swell considerably, and retain two to three times as much water as coarser fibers.

In regard to retention, electrophoresis measurements involve only fines and not the fiber. It has long been a controversial assumption that the electrokinetic charge on the fines is representative of the entire fiber system. A study done by Hinton and Quinn (20) seems to suggest that the zeta potentials of fibers, classified according to their fiber length, increase with decreasing fiber size. Fiber fines which pass through a 200 mesh screen are reported to possess approximately three times higher electro-negative zeta potentials than those of long fibers. Contrary to this finding, Strazdins (23) postulated that the zeta potential of fines agrees with the zeta potential of the fibers from which the fines originated.

A study done by Williams and King revealed that fiber-to-fiber flocculation depends highly on fines addition levels (24). In this study they found that the test polymers were effective flocculants in different ways. The fiber-to-fiber systems showed maximum degrees of flocculation at a certain polymer concentration, with fiber redispersion occurring upon increased polymer addition. However, although the polymers induced fines flocculation to the fibers, the fines remained attached to the fibers past the polymer

concentrations where the fibers became redispersed. This result is significant, since it demonstrates that maintaining the desirable condition of good fiber dispersion, while still maintaining good fines retention, is possible.

A study done by Jaycock (8) examined a system of titanium dioxide and other additives with fines. The zeta potentials of just the pigments, just the fines, and a system of both pigment and fines were taken. Different isoelectric points were determined for fines alone and titanium dioxide alone. When titanium dioxide was combined with fines, the isoelectric point was very near the point for fines alone.

PRESENTATION OF THE PROBLEM

Many studies have considered the effects of shear, polyelectrolyte addition, and pH on paper machine retention. This study will attempt to determine a correlation between fiber furnish length and retention of titanium dioxide pigment under various levels of retention aid and shear.

EXPERIMENTAL PROCEDURE AND CALCULATIONS

Pulp Preparation

A 50% hardwood kraft - 50% softwood kraft furnish was prepared in a Hollander Beater and beaten to a CS freeness of 500. Consistency measurements were made by measuring a known quantity of stock and pouring it through a Buchner funnel with pre-weighed Whatman #40 filter paper. The filter paper was then dried in a

circulating air oven to a constant weight. The fiber consistency was calculated according to the following formula:

$$\% \text{ Consistency} = \frac{(\text{Weight of Filter Paper} + \text{Filtrate})}{\text{Weight of Total Paper}} - \frac{(\text{Weight of Filter Paper})}{(\text{Approximately } 100 \text{ ml})} \times 100$$

The pulp sample was then fractionated in a Clark Fiber Classifier according to TAPPI Standard T . Screen sizes used in the classifier were 10, 35, 50, and 100 mesh respectively. Fiber samples were collected from the second, third, and fourth compartments by wrapping the outlets with muslin. Following the classification, each respective fiber length was checked for consistency by the same method described earlier. Twenty percent TiO_2 by weight of fiber was then added to each fiber length. The TiO_2 was added into the fiber in the beater with all of the weights removed and was allowed to mix in for five minutes.

Zeta Potential Measurements

Samples of each fiber length were withdrawn previous to the TiO_2 addition. These samples were used for zeta potential measurements using the Lazer Zee meter.

A measurement of the zeta potential and specific conductance of the standard colloid was then performed. The standard cell was cleaned by soaking the cell in the supplied cleaning solution for 24 hours. The cell was then rinsed several times with distilled water. A 30 ml syringe was used to deliver 25 ml of the standard colloid into the cell. The cell was then placed into the meter. After turning the power on, the voltage was adjusted to 150 volts. The stationary layer was then found by focusing at the inner top surface of the cell, and then rotating the course focus knob a valve equal to the cell constant (218 μm) in order to focus at

the stationary layer. The laser was then adjusted to give optimum viewing, and the zeta potention knob adjusted (after pushing the high voltage button) to the isoelectric point voltage. The average reading of four runs yielded a value of -33.6 mv, which is 1.2% away from the known value. The zeta potential of TiO_2 in the mother liquor (tap water) was then obtained in a similar manner. An average of four runs yielded a value of -20.3mv and a specific conductance of 423 umhos.

A solution of Betz 1260 high molecular weight cationic retention aid was prepared at a concentration of 0.05% by weight water, the water used was obtained from the Clark Classifier. The polymer was added to a weighed amount of water and was dispersed at low shear with an agitator for approximately 16 hours.

The zeta potentials of different solutions of TiO_2 and cationic retention aid were taken and the results recorded. The level of addition of retention aid that resulted in a zeta potential of zero was found. This level of retention aid was used as the isoelectric point addition.

TiO_2 Retention

The Dynamic Drainage Jar was used to determine the TiO_2 retention of each of the fiber samples.

The different fiber samples were kept dispersed with an agitator. The amount of pulp needed to obtain a consistency of 0.5% in 500 ml stock total was calculated. Three different levels of retention aid were used: 0.001 lb/ton, 0.1 lb/ton, and 0.2 lb/ton. Three different levels of shear were also used; 1000, 2000, and 3000 R.P.M.

For each respective fiber length, the proper amount of stock with TiO_2 was introduced into the Dynamic Drainage Jar. The stirrer was set at 300 R.P.M. and the contents were allowed to mix for 30 seconds. An air pressure of 6 oz/in² was introduced into the bottom of the jar in order to keep the stock from draining prematurely into the drainage zone. This pressure was equal to the head pressure ($P=h\rho$). After 30 seconds, the stirrer was accelerated to the respective speed and the cationic retention aid was added. The contents were allowed to mix for 15 seconds. At the end of the 15 seconds, the first 100 ml were drained into a pre-weighed 125 ml beaker. The contents plus the beaker were then weighed and filtered through a pre-weighed Whatman glass microfibre filter paper, which was the only filter paper found that could retain the TiO_2 . The paper was then placed in a muffle furnace at 600 degrees centigrade for 20 minutes, removed, placed in a dessicator, and then weighed. The percent retention of TiO_2 was calculated with the following equation:

% Retention (TiO_2) =

$$\frac{\left[\frac{\text{Weight of Aliquot}}{\text{Total Wt. of Sample}} \times \text{Total Wt. of } \text{TiO}_2 \text{ in Total Sample} \right] - (\text{Wt. of Filter Paper} + \text{Ash} - \text{Wt. of Filtered Paper})}{\left(\frac{\text{Weight of Aliquot}}{\text{Total Wt. of Sample}} \times \text{Total Weight of } \text{TiO}_2 \text{ in Total Sample} \right)} \times 100$$

RESULTS AND DISCUSSION

Zeta Potential Measurements

The zeta potential and specific conductance of the various solutions tested are listed in Table 2.

Table 2

<u>Substance Checked</u>	<u>Medium</u>	<u>Retention Aid (lbs/ton)</u>	<u>Z.P. (mv)</u>	<u>S.C. (umhos)</u>
TiO ₂	Distilled H ₂ O	0	-34.6	109
TiO ₂	Mother Liquor	0	-20.3	423
TiO ₂	Mother Liquor	0.2	+12.3	451
TiO ₂	Mother Liquor	0.1	+12.1	447
TiO ₂	Mother Liquor	0.067	+11.8	446
TiO ₂	Mother Liquor	0.033	+10.5	444
TiO ₂	Mother Liquor	0.0067	+8.8	440
TiO ₂	Mother Liquor	0.0026	+4.0	440
TiO ₂	Mother Liquor	0.001	+0.0	438

The isoelectric point of TiO₂ in the mother liquor was found to be at a retention aid level of 0.001 lb/ton.

Retention

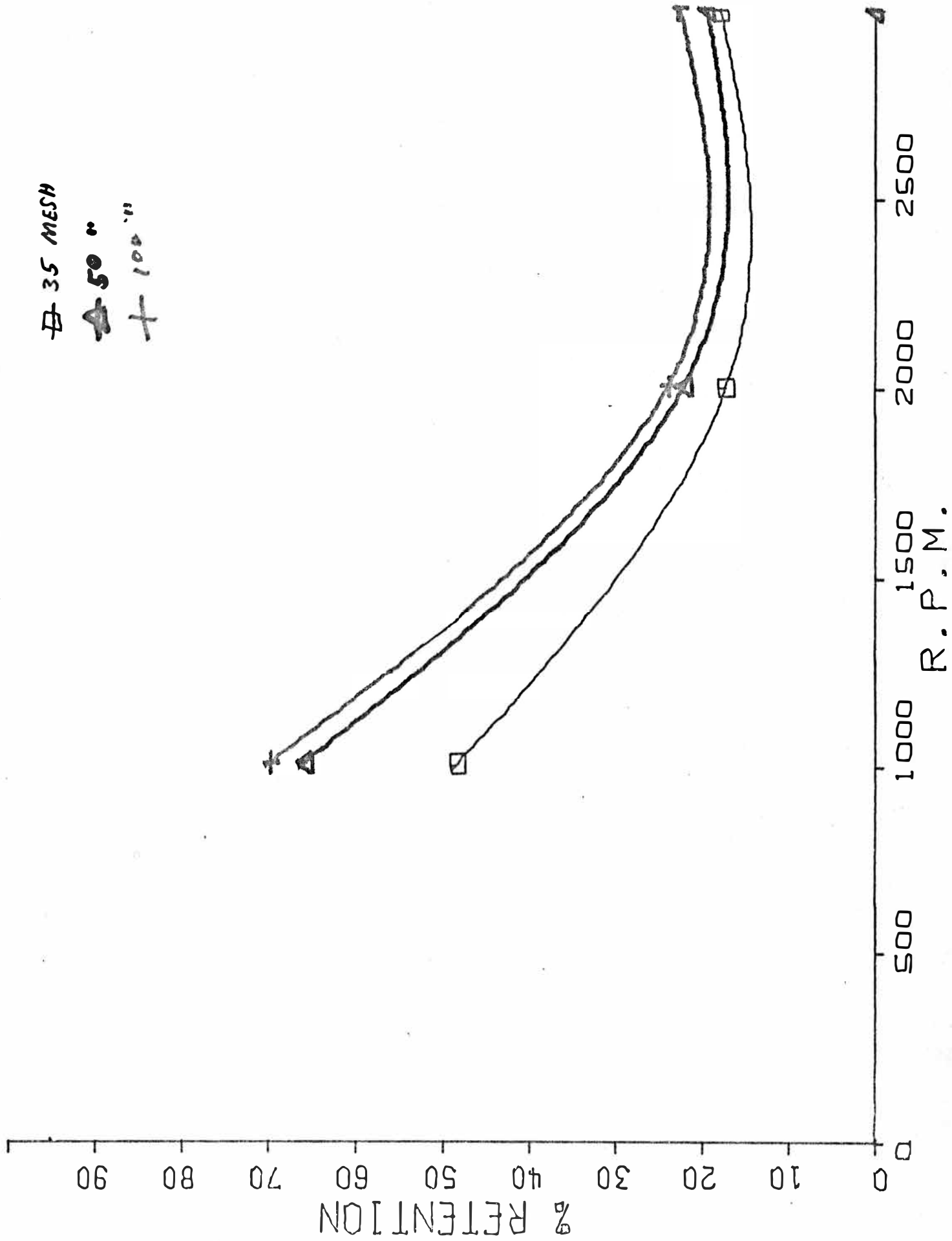
Data for the mean retentions for each fiber distribution are listed in Table 3.

Graphs of % retention vs. revolutions per minute for 0.001 lb/ton, 0.1 lb/ton, and 0.2 lb/ton are given in Figures 3, 4, and 5, respectively. The three fiber lengths on each graph are color coded and are 35 mesh (longest), 50 mesh, and 100 mesh. As can be seen from the graphs, a trend of improved retention as the fiber length decreased is implied at all rates of shear.

Figure 3

0.001 lb/ton

35 MESH
50 "
100 "



0.1 lb/ton

35 MESH
50 "
100 "

Figure 4

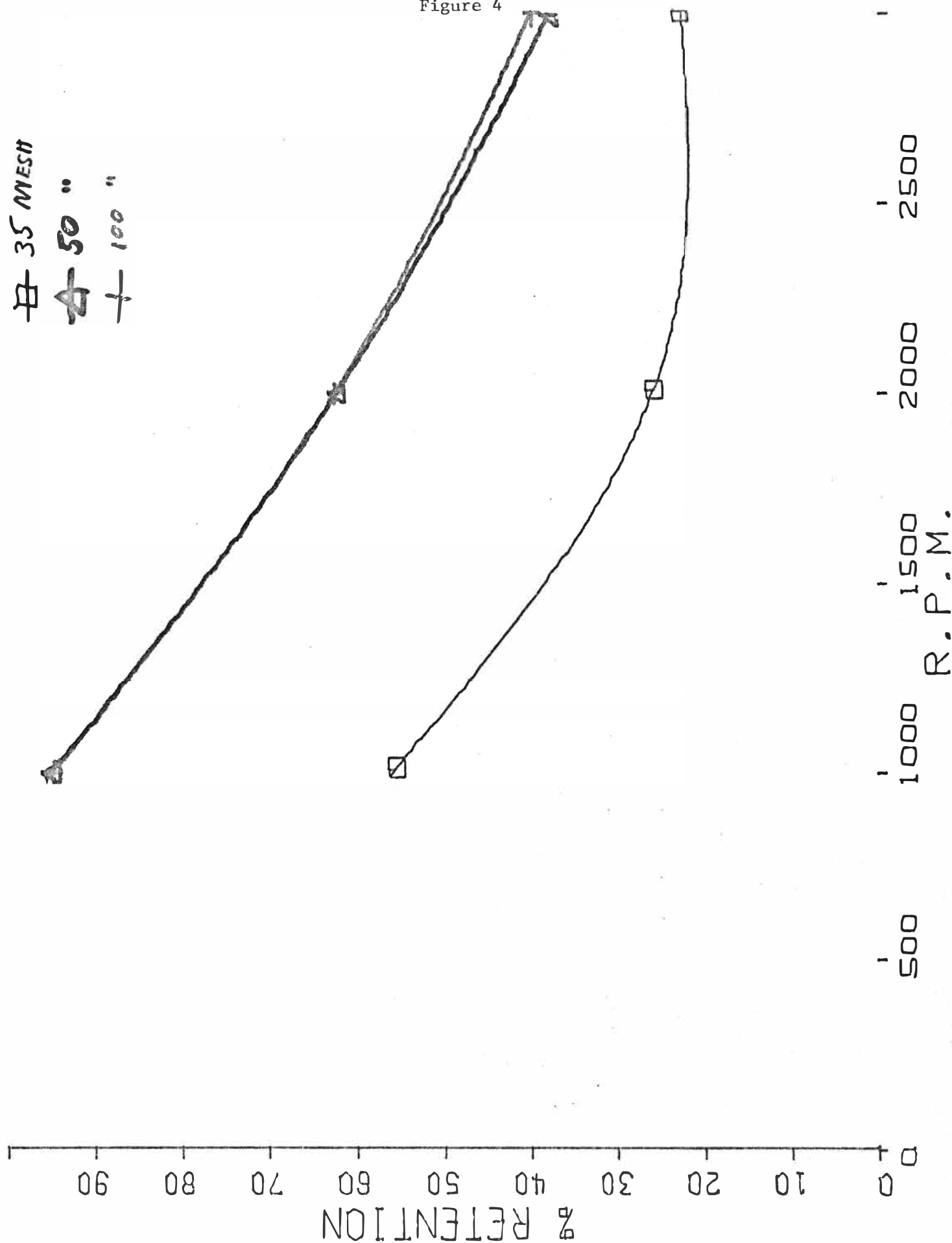


Figure 5

0.2 lb/TON

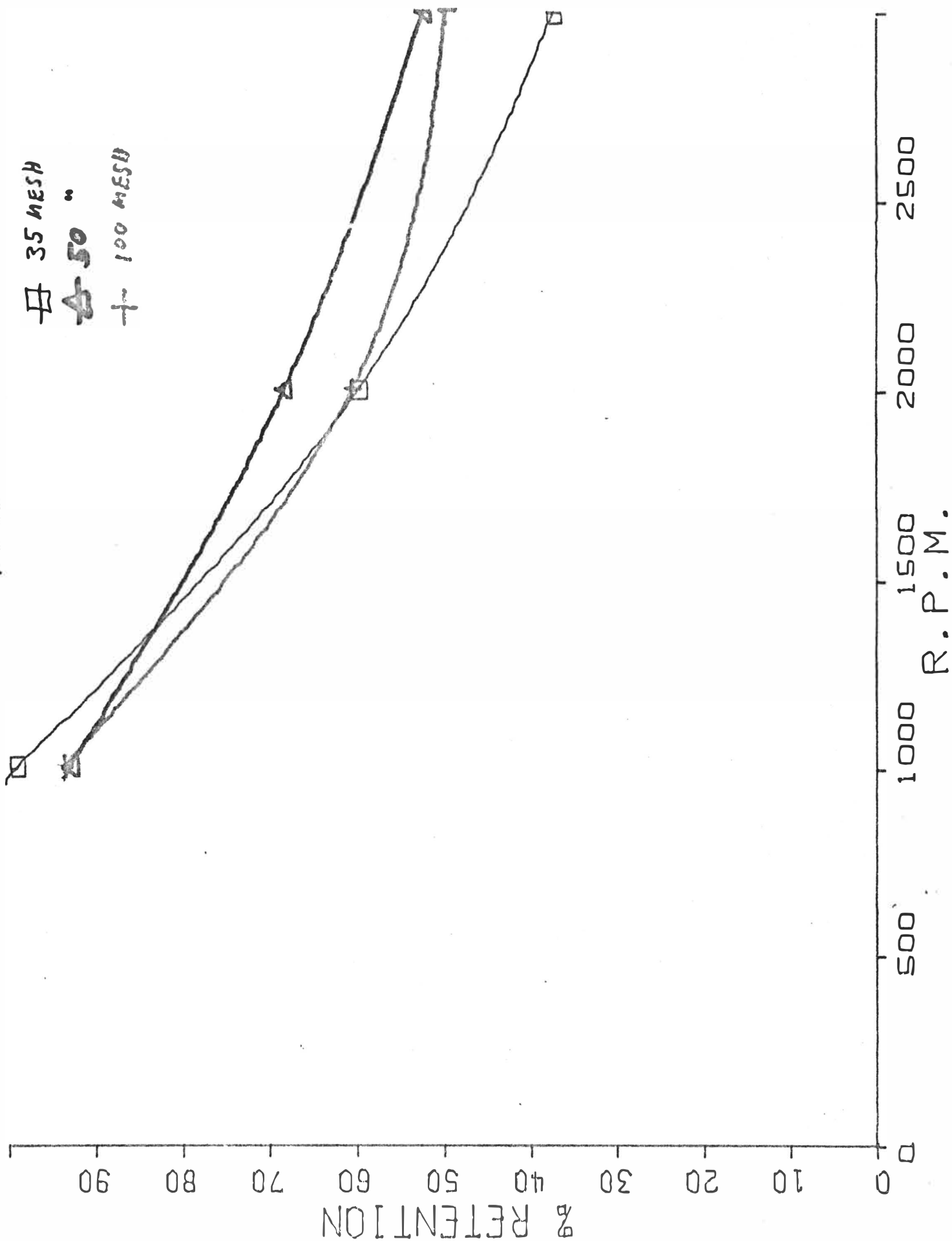


Figure 6

% RETENTION VS. LEVEL OF ADDITION
(WHOLE PUMP)

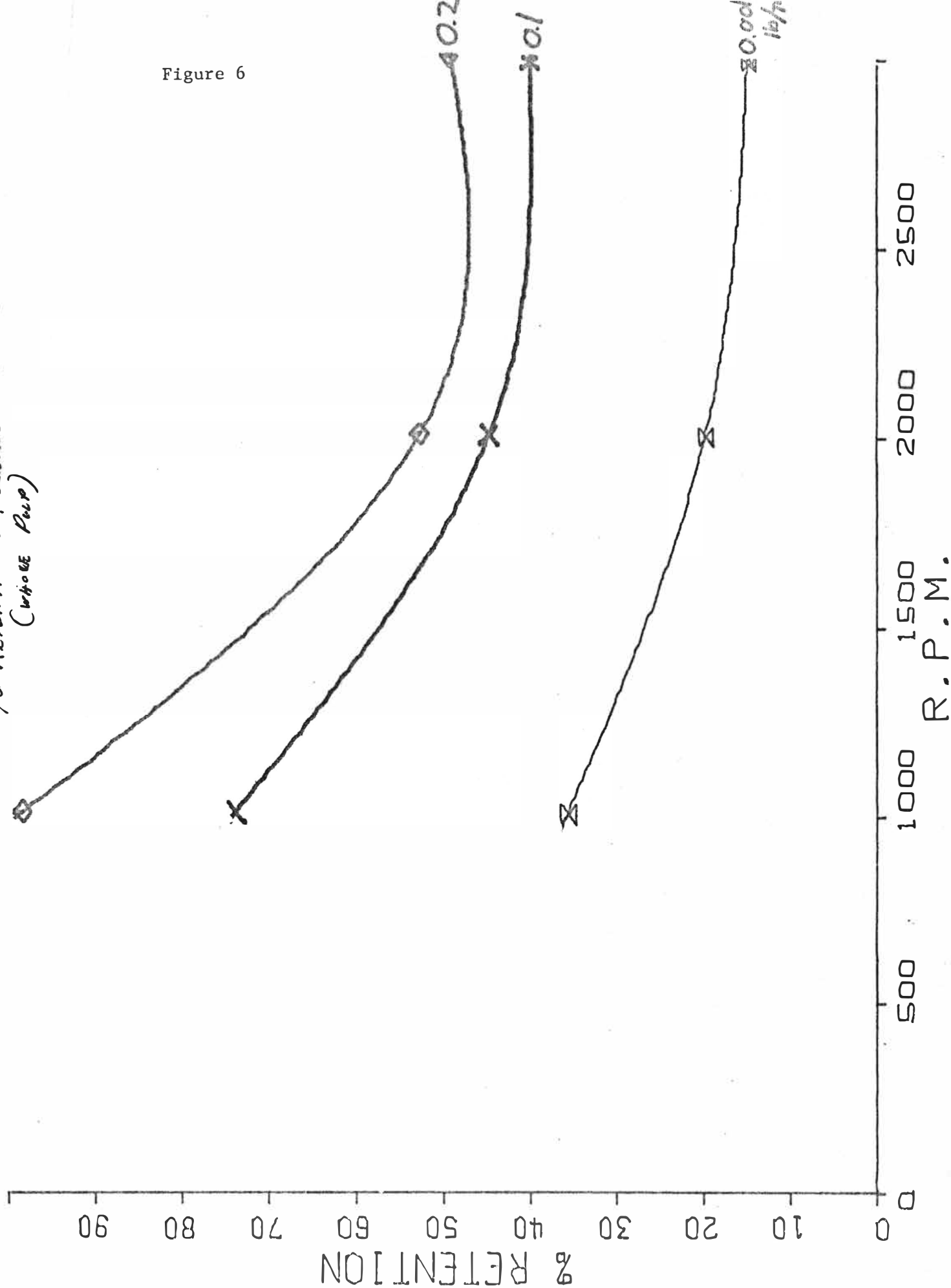


Table 3

% Retention (TiO_2)

	<u>Whole Pulp</u>	<u>Fines</u>	<u>35 Mesh</u>	<u>50 Mesh</u>	(1 Run) <u>100 Mesh</u>
<u>Control (0 R.A.)</u>					
1000 R.P.M.	15.39 \pm 1.2	Mat Formed	39.14 \pm 1.3	37.04 \pm 1.1	38.60
2000 R.P.M.	15.36 \pm 1.4	6.48 \pm 5.4	12.88 \pm 1.4	19.51 \pm 1.9	19.81
3000 R.P.M.	17.35 \pm 0.8	4.65 \pm 3.1	12.31 \pm 0.7	15.35 \pm 2.2	16.06
<u>0.001 lb/ton</u>					
1000 R.P.M.	35.71 \pm 2.6	22.01 \pm 10.2	48.32 \pm 2.6	65.66 \pm 4.1	69.48
2000 R.P.M.	19.72 \pm 1.9	14.94 \pm 8.1	17.23 \pm 1.3	21.89 \pm 2.2	23.61
3000 R.P.M.	14.86 \pm 1.1	2.02 \pm 1.6	17.95 \pm 1.6	19.29 \pm 3.6	22.36
<u>0.1 lb/ton</u>					
1000 R.P.M.	73.86 \pm 2.1	97.97 \pm 2.1	55.42 \pm 2.0	94.49 \pm 3.2	94.20
2000 R.P.M.	44.73 \pm 1.6	75.14 \pm 8.6	25.90 \pm 1.8	61.78 \pm 2.3	62.01
3000 R.P.M.	40.14 \pm 1.2	23.86 \pm 9.2	22.94 \pm 3.6	37.63 \pm 2.9	39.68
<u>0.2 lb/ton</u>					
1000 R.P.M.	98.07 \pm 0.8	99.26 \pm 0.3	98.88 \pm 0.6	92.72 \pm 4.6	93.35
2000 R.P.M.	52.58 \pm 3.1	60.09 \pm 8.2	59.64 \pm 3.4	68.12 \pm 3.1	60.12
3000 R.P.M.	49.18 \pm 2.2	4.57 \pm 3.2	37.31 \pm 2.6	52.08 \pm 6.4	49.45

The effect of increasing the level of retention aid can be seen both from Table 3 and from Figure 6. The highest level of retention aid provided the highest retention of TiO_2 . The level of addition that provided the lowest level of retention (excluding the control) was the 0.001 lb/ton level of addition, which was also the level of addition that supplied an isoelectric point for the system. According to Penniman, the level of addition that achieved the isoelectric point should have provided optimum flocculation. Analysis of the data obtained suggests that an alternate mechanism was responsible for retention.

The bridging mechanism (4) could account for the results in retention. The bridging mechanism suggests that one end of the polymer molecule attaches itself to the particle in suspension,

and the other end remains dangling in solution. When another similar particle approaches, the dangling ends of the polymers attach themselves to the other particle, thus forming a "bridge" between the two particles. This mechanism would account for the fact that better retention was obtained at levels of addition 200 times higher than the isoelectric point level of addition.

The fines fraction of the pulp sample gave very poor reproducibility. This was due to the glass melting around the fiber fines and not allowing complete combustion. Due to the high standard deviations obtained, the data was not considered and an additional run of 100 mesh fiber was substituted.

CONCLUSIONS

1) Optimum retention of TiO_2 was achieved at a level of addition 200 times the calculated optimum addition level (isoelectric point). This may suggest that the bridging mechanism was the dominant mechanism for flocculation in this system.

2) Shorter fibers supply better retention of TiO_2 than longer fibers under equal conditions of retention aid level and shear. This may be due to better bridging characteristics between the smaller fibers than the larger fibers. The smaller fibers possess a larger surface area for bridging to occur, thus providing a more stable floc.

RECOMMENDATIONS

- 1) Further work be done with fiber fines (≤ 200 mesh) so as to determine their effect on TiO_2 retention.
- 2) Further research be done with different pigments or fillers, such as clay or calcium carbonate.
- 3) Further research be done on the relationship between flocculating mechanisms (i.e., bridging, electrostatic considerations).
- 4) Further research be done using a variety of retention aids.
- 5) A flocculation curve of TiO_2 could be obtained (i.e., a level of cationic retention aid that causes re-dispersion of the TiO_2).

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