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## The Effect of Various Initial Electrokinetic Potentials on the Retention of Titanium Dioxide

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The Effect of Various Initial  
Electrokinetic Potentials on the Retention  
of Titanium Dioxide

by  
Jeff L. Gutowski

A Thesis submitted to the  
Faculty of the Department of Paper Technology  
in partial fulfillment  
of the  
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Western Michigan University  
Kalamazoo, Michigan

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## Abstract

The purpose of this thesis was to find out if maximum  $\text{TiO}_2$  retention will always occur in an electrokinetic range of  $+3$  mV, as theorized, regardless of initial electrokinetic values. The systems investigated, included the addition of 5%  $\text{TiO}_2$  slurries at various positive and negative electrokinetic values to pulp slurries, also at various charges. Even though all 13 systems investigated by handsheet analysis were all run at the same final electrokinetic values of  $\pm 4$  mV, wide variations in their % retention of  $\text{TiO}_2$  were found. The scattering coefficient of  $\text{TiO}_2$  and the conductivity and % light transmission of the water filtrate were also obtained and analyzed for each individual system. Conductivity remained fairly constant in all of the systems, with % light transmission, increasing with an increase in % retention. Scattering coefficients were somewhat higher in those systems having lower % retention.

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## Historical Background

Since the late 1940's there has been considerable study concerning the effect of zeta potential in paper-making operations. A consensus of investigators has found that wet-end chemistry, which includes: formation, sizing, fines retention, pigment retention, opacity, wet strength, dry strength, pitch, dye retention, and drainage, is markedly affected by those paper making additives which change the zeta potential of the system.<sup>1</sup>

Zeta potential may be simply defined as surface charge density and is expressed in millivolts. Colloids in nature are negatively charged. The more negative, or the higher the zeta potential, the greater the repulsion and therefore the greater the stability. The converse is true, and as the zeta potential approaches zero, the negative charge becomes less effective and conditions approach optimum for flocculation and consequent precipitation.

For a much more in-depth technical definition, we need to learn about the structure of the electrical double layer which have contributed to the explanation of many phenomena of the chemistry of colloids. The first layer is firmly located on the surface of the dispersed phase, and the second is located in the dispersing agent. The formation of such an electrical double layer on the interface of a solid and liquid phase was proposed by H. Helmholtz (1879). Helmholtz

postulated that the formation of such a layer occurs at any interface of a layer. In his opinion, a sheet-like electrical layer consisting of ions is formed also<sup>1</sup> in the solution opposite the sheet-like charged layer, bound to the surface of the solid phase.<sup>2</sup>

A closer study of Helmholtz's ideas of the molecular double layer sometimes fail to represent the actual conditions and that the double layer apparently extends deeper into the solution. Such a double layer is called a diffuse layer and has been described by Gouy and Chapman. This layer at the interface of a solid phase and a solution results from the effect of two influences opposing each other, while the electrical forces effect to form a double layer as envisioned by Helmholtz, <sup>3</sup> these forces are opposed by the molecular thermal motion which tends to distribute the ions equally in the surrounding solution. The diffuse double layer can also be regarded as a flat plate condenser.<sup>3, 4</sup>

Discrepancies were found in their theories by O. Stern who combined both their ideas and thus created the theory of a composite double layer which corresponds best to actual conditions. According to Stern,<sup>5</sup> the electrolytic double layer is therefore divided into a rigid double layer (Helmholtz Layer) and into a diffuse double layer, in which part of the counter ions remain in a compact layer on the charged colloid surface as a consequence of the existence of strong electrostatic

forces as well as Van der Waals forces. The other part of the counter ions extends into the bulk of the solution and constitutes the so called Gouy-Chapman diffuse layer.

The potential difference which corresponds to the diffuse part of the electrical double layer, has an important function, particularly in all of those processes in which there is a relative motion of the solid phase in relation to the solution. During this motion, the liquid is not displaced directly along the surface of the solid phase, but a monomolecular layer of the solvent with absorbed ions is attached to the surface, while at the same time a deformation of the double layer appears. The contact surface of the motion under consideration is therefore exactly the interface between Helmholtz's layer and the diffuse double layer. The potential difference between the interface and the core of the solution, is called electro-kinetic potential or the zeta potential. If this electric potential is reduced, then the repelling forces become weaker and the constant Van der Waals forces of attraction will become more important. At the isoelectric point, in which the ZP is zero, no repelling forces are active and the particles conglomerate as a consequence of the Van der Waals forces and then flocculate. This is the condition we want going onto the paper machine wire. For at this isoelectric point



we obtain improved drainage, improved physical properties, but more importantly maximum retention, which due to the rising costs of fillers, especially TiO<sub>2</sub>, (analyses of paper mill effluents have shown losses as high as \$2.00/ton) will be a major concern of this paper.

Sennet<sup>6</sup> feels that the physical effects of the electrical double layer in reference to zeta potential, are insignificant when dealing with systems where the surface area in contact is very small compared to the mass of the components in the system. Only when the interfacial areas are relatively large will the electrical double layer effects become important and significant. With reference to filler retention, the latter case definitely applies since in a well dispersed TiO<sub>2</sub> solution, the filler particles are very small, on the order of .2 microns. It is agreed that there are several factors which affect filler retention besides the zeta potential. According to McKenzie and Davies,<sup>7</sup> all of the following are important: formation of polymer bridges between the components, formation of mixed colloidal aggregates in presence of alum, and the ability of the fiber-additive aggregates to withstand the hydrodynamic shear forces operating during furnish preparation and sheet formation.

Cellulose fibers, which comprise the major portion of the furnish, have a negative zeta potential. This charge becomes more negative for higher lignin content

pulps. Inorganic pigments and fillers such as titanium dioxide and clay usually are dispersed prior to being mixed with the stock by a phosphate dispersing agent which imparts a high negative zeta potential to these pigments as well. In order to confer this charge cationic retention aids are added. They serve the dual function of charge neutralization and simultaneous flocculation via the bridging mechanism. Since they lower the pH, the more positive the zeta potential becomes, they have the advantages of less pH dependence than alum and higher sensitivity of use.<sup>8</sup>

The quality of process water is also important in controlling zeta potential. Dissolved salts will cause the zeta potential to decrease in magnitude. The effect of salt is always to move the zeta potential toward zero. Therefore water hardness and sulphate ion concentration become important parameters in the control of zeta potential.<sup>9</sup> The pH of the system is also important due to the fact that, the lower the pH, the more positive the zeta potential becomes.

It can also be seen that  $TiO_2$ , which at a pH value under 6, shows a positive zeta potential with cationic flocculation agents like alum, will yield an unsatisfactory retention. By adding 1.8% of sodium aluminate solution, the retention of  $TiO_2$  in an industrial test was increased to 88% as opposed to 50%, which was the case during the earlier production process. This

retention increase can be attributed to the interacting of several effects. Through the alkaline reaction of the aluminate, the ZP of the  $\text{TiO}_2$  is shifted into a stronger negative region.  $\text{TiO}_2$ , due to its ZP, tends to disperse easily, and because of this, a good original dispersion is accomplished. The more the filler material is dispersed, and the more they are available in their primary particles, the better is the resulting retention.<sup>10</sup>

Zeta potential measurement is essential in determining the proper retention charge type and the optimum level to use. Too much polymer will redisperse the system and reduce retention.

A maximum agglomeration or flocculation takes place in a zeta potential range from 3mv to zero. This range of precipitation is necessary for a favorable retention. Simple control over the zeta potential, is, however, not sufficient for an effective flocculation. The nature of coagulation is also caused by the energetic influences of thermal and mechanical energy. A rise in temperature in general promotes flocculation by increasing brownian motion and the increased collision associated with it. The flocculation by agitation is considerably different in hydrosols low in electrolytes to the ordinary electrolyte flocculation. The valence influences of flocculating ions are much greater in agitated sol than in beaten sol. To obtain an efficient flocculation, it is necessary to have rapid agitation

initially and slow stirring toward the end.<sup>11</sup>

The methods used today for the determination of the electro-kinetic potential are: electro-osmosis, the electro-osmotic pressure, streaming potential, and electrophoresis. All methods use the influence of a potential or pressure gradient on the system, where, e.g. small charged particles migrate in a system under the influence of the electrical field. By measuring the velocity of the migration, we can calculate the zeta potential with the appropriate formula.<sup>12</sup> All of these provide good measurement of zeta potential but have several drawbacks to the average paper mill personnel. First, most of them are complicated and require a great deal of understanding to actually obtain accurate and reproducible results. Secondly, most of these methods are tedious and time consuming in that great care must be taken to make sure that every little thing is in exact working order with an emphasis on cleanliness. Thirdly, these instruments, due to their complexity and expense, are quite fragile so that frequent recalibration and repairing is necessary. Also the streaming current detector does not work well with slurries since the fibers and fillers will prohibit proper motion of the piston and boot, thereby making true readings difficult. As a result of these difficulties, many papermills tend to shy away from measuring zeta potential. So there is a definite need

for a practical device which will accurately and continually measure zeta potential. Since the zeta potential of a paper making system is dependent on a large number of variables, including: fiber and filler type, pH, alum dose, polymer addition, wet-end additives and water quality, a continuing measuring device is needed due to tremendous surging changes of zeta potential. Changing one of the above variables will change others in ways that are impossible to predict in the absence of continuing zeta potential measurements.

One approach which looks promising for a continuous measuring system was developed by Dorchak<sup>13</sup> who found that at the pH of zero zeta potential, a starch sol exhibits a transmission minimum. In other words, by continually titrating a starch solution with an appropriate polyelectrolyte, and then taking transmission readings on a spectrometer, the decrease in zeta potential and the reaching of the isoelectric point can actually be followed by a decreasing transmission until a minimum in the transmission is obtained. At this transmission and concentration of additives, the zeta potential of the system will be zero and upon further addition of polyelectrolyte, the transmission will start to increase. This seems feasible since at the isoelectric point, flocculation will occur but more importantly, particle density will be at a

maximum since there will be no charge present trying to make the particle expand.

Myers<sup>14</sup> supported this work when he titrated starch solutions with NaOH to a minimum in transmission and then used a streaming current detector to measure the zeta potential. He found that the zero zeta potential correlated very well with the transmission minimum.

Other promising work was done by A.P. Black, F.B. Birkner, and J.J. Morgan<sup>15</sup> who made a detailed study of the destabilization of dilute clay suspensions with cationic polymer. They found that the measurement of the destabilization of the system could be determined by a measurement of the residual turbidity of the precipitated suspensions. The optimum stabilization occurred at a ZP equal to zero.

E. Matijevic, G. Janauer and M. Kerker<sup>16</sup> investigated the charge reversal of lyophobic colloids due to hydrolized metal ions. As measuring devices, they use the light scattering of the solutions, which is proportional to the turbidity if the particles are small and electrolytes are sufficiently diluted. In this manner, the authors determined the critical stabilization concentration and the dependency of the electrolyte concentration.

Peterson<sup>17</sup> created a new and easy testing procedure for determining relative strengths of cationic retention aids. His theory was based on the relation between turbidity and zeta potential of a starch

solution. A .1% starch sol was produced and then titrated with various .1% retention aid solution. After each incremental addition of retention aid, a zeta potential reading and a transmission reading were taken. Good correlation was discovered between the isoelectric point and the transmission minimum. The relative amounts of retention needed to obtain this transmission minimum were an indication of the charge that the retention aids possessed. This test has several benefits to the papermaker, among which are: very short time necessary to actually run the test, ease of operation as far as complexity of instruments and measurements are concerned, and the low cost of the test since all apparatus necessary is already in most paper laboratories.

A continuous measurement of zeta potential in order to control your retention, seems to be right around the corner.

## Experimental Objective and Design

After years of research and experimentation on zeta potential and its relationship to retention, it is now become an established supposition that maximum pigment retention occurs in a range of -3 millivolts to +3 millivolts. The objective of this thesis is to find out if this is always the case that maximum retention occurs in this range, regardless of the initial electrokinetic values. The systems to be investigated would include the addition of 5% (by ash content)  $\text{TiO}_2$  slurries at various positive and negative electrokinetic values to pulp slurries also at various values. The adjustment to these different electrokinetic values will be made either by the addition of Merck Hydraid 7300-C (high molecular weight, anionic polyelectrolyte at .1% solids) or by Merck Hydraid 261 (low molecular weight, cationic polyelectrolyte at .1.3% solids) depending on what charge is desired.



### Experimental Procedure

Rayonier bleached softwood kraft pulp was used as the fiber base. Five percent Rutile  $\text{TiO}_2$  was dispersed in a waring blender for 5 minutes at low speed. The pulp and  $\text{TiO}_2$  slurries were separately adjusted in distilled water to the desired charge and then blended together for the making of 2.54 gram handsheets on the Noble and Wood sheet mold. The white water from each system (filtrate through a 100 mesh screen) was tested for conductivity and % light transmission. The Spectronic 20 Colorimeter was used for light transmission measurement at a wavelength of 457 millimicrons. All electrokinetic potential readings were obtained on the Waters Associates Streaming Current Detector, which will be abbreviated henceforth as SCD.

#### Procedure for Streaming Current Detector

1. A standard solution (.1 Molar NaCl) to which the instrument can be calibrated was prepared.
2. Immerse boot and piston in standard until liquid is above the cut-out opening in the boot.
3. Push power switch to the ON position.
4. When first starting, turn sensitivity selector switch to X-20, which is the least sensitive position.
5. Push motor switch to the ON position. A 3 minute timing period was used.
6. Observe the meter reading.
7. If the reading on the meter is very small, adjust the

sensitivity selector switch to a more sensitive position.

8. When the reading has stabilized after adjusting to zero, the measuring head should be raised out of the solution after the motor switch has been turned off.

9. Boot is removed and vigorously scrubbed along with the piston and electrode with a stiff nylon test tube brush and a 1% Essex gum cleaning solution. Scrubbed surfaces then rinsed thoroughly in distilled water.

10. Steps 1-9 were followed replacing the standard with the sample solutions being tested.

#### Optical Tests

Brightness and opacity were taken on the hand sheets made for each individual system, so the scattering coefficients of  $\text{TiO}_2$  could be obtained.

## Data

All pulp slurries were made by the addition of 10 grams of Rayonier pulp in 1000 ml of distilled water. All  $\text{TiO}_2$  slurries were made by the addition of .5 grams of Rutile  $\text{TiO}_2$  in 1000 ml of distilled water. The numbers 261 and 7300-C, which will both be used repeatedly in the data below, represent the cationic and anionic Merck Hydraids, respectively. The data is arranged in decreasing order of % retention of  $\text{TiO}_2$ .

System # 1       $\text{TiO}_2$  slurry plus addition of 12 drops of 7300-C to obtain a SCD reading of -64 mV, mixed together with the pulp slurry which was at +54 mV, brought about by addition of 35 drops of 261. Total combined reading of +40 mV, so added 76 ml of 7300-C to obtain final reading of -2.4 mV. Handsheets were then made at this final reading.

System # 2       $\text{TiO}_2$  slurry plus .1% Calgon T to obtain SCD reading of -58 mV, mixed together with the pulp slurry which is at +59 mV brought about by addition of 15 drops of 261. Total combined reading of +28 mV, so added 15 ml of 7300-C to obtain final reading of +4.0 mV.

System # 3       $\text{TiO}_2$  slurry plus 11 drops of 261 to obtain SCD reading of +66 mV, mixed together with the pulp slurry which is at -62 mV, brought about by addition of 14 ml of 7300-C. Total combined reading of +22 mV, so added 6 ml of 7300-C

to obtain final reading of  $\sim 3$  mV.

System # 4       $\text{TiO}_2$  slurry plus 11 drops of 261 to obtain SCD reading of +61 mV, mixed together with pulp slurry which is at -2 mV, brought about by addition of 4 drops of 261. Total combined reading of +37 mV, so added 8 ml of 7300-C to obtain final reading of +1.4 mV.

System # 5       $\text{TiO}_2$  slurry plus 3 drops of 261 to obtain SCD reading of +37 mV, mixed together with pulp slurry which is at +42 mV, brought about by addition of 13 drops of 261. Total combined reading of +37 mV, so added 19.5 ml of 7300-C to obtain final reading of -1.0 mV.

System # 6       $\text{TiO}_2$  slurry plus .1% Calgon T, plus 17 drops of 7300-C to obtain SCD reading of -59 mV, mixed together with the pulp slurry which is at +4 mV, brought about by addition of 5 drops of 261. Total combined reading of -24 mV, so added 17 drops of 261 to obtain final reading of -3 mV.

System # 7       $\text{TiO}_2$  slurry plus 2 drops of 261 to obtain SCD reading of 0 mV, mixed together with the pulp slurry which is at -.2 mV, brought about by addition of 4 drops of 261. Total combined reading and also the final reading was at -4.0 mV.

System # 8       $\text{TiO}_2$  slurry plus 3 drops of 261 to obtain SCD

reading of +29 mV, mixed together with the pulp slurry which is at -26.5 mV, as is. Total combined and final SCD reading was at +1.6 mV.

System # 9       $\text{TiO}_2$  slurry, as is, gave a -31.0 mV reading, mixed together with the pulp slurry which is at +30 mV, brought about by addition of 10 drops of 261. Total combined reading of +7.3 mV so added 1.8 ml of 7300-C to obtain final reading of -2.0 mV.

System # 10       $\text{TiO}_2$  slurry plus 4 drops of 261 gave a +39 mV reading, mixed together with the pulp slurry at -44 mV, as is. Total combined reading of -22 mV. so added 5 drops of 261 to obtain final reading of +.6 mV.

System # 11       $\text{TiO}_2$  slurry plus 3 drops of 261, plus 56 drops of 7300-C to obtain -3 mV reading, mixed together with the pulp slurry which is at a -4 mV reading by addition of 6 drops of 261 plus 11 drops of 7300-C. Total system reading of -19 mV, so added 2 drops of 261, plus 8 drops of 7300-C, to obtain final reading of -2.6 mV.

System # 12       $\text{TiO}_2$  slurry, as is, gave a -64 mV reading, mixed together with the pulp slurry which was at -71 mV, as is. Total combined reading of -61 mV, so added 10 drops of 261 to obtain final reading of -2.0 mV.

System # 13       $\text{TiO}_2$  slurry, as is, gave a -45 mV reading, mixed together with the pulp slurry which was at a +30 mV reading by

addition of .05% of 261. Total system reading of +22 mV, so added 10 drops of 7300-C to obtain final reading of -2.2 mV.

Additional data included the control handsheets (no  $\text{TiO}_2$  or polyelectrolyte added) which gave a brightness of 85.2%; an opacity of 75.8% and an ash content of .37%.

SYSTEM	1	2	3	4	5
	TiO <sub>2</sub> -64 pulp +54 FINAL READING AT -2.4	TiO <sub>2</sub> -58 pulp +59 FINAL READING AT +4.0	TiO <sub>2</sub> +66 pulp -62 FINAL READING AT -3.0	TiO <sub>2</sub> +61 pulp -2 FINAL READING AT +1.4	TiO <sub>2</sub> +37 pulp +42 FINAL READING AT -1.0
CONDUCTIVITY MHOS	44	31.2	24	30	30
LIGHT TRANSMISSION %	86	71	83	85	52
BRIGHTNESS %	89.7	88.1	92.1	90.5	87.2
OPACITY %	83.2	82.9	81.3	81.9	80.8
SCATTERING COEFFICIENT	.56	.66	.44	.40	.45
RETENTION %	82.6	79.5	78.7	78.3	70.4

NOTE

6	7	8	9	10	11	12	13
TiO <sub>2</sub> -59 pulp +4 FINAL READING AT -3.0	TiO <sub>2</sub> 0 pulp -.2 FINAL READING AT -4.0	TiO <sub>2</sub> +29 pulp -26.5 FINAL READING AT +1.6	TiO <sub>2</sub> -31 pulp +30 FINAL READING AT -2.0	TiO <sub>2</sub> +39 pulp -44 FINAL READING AT +.6	TiO <sub>2</sub> -3 pulp -4 FINAL READING AT -2.6	TiO <sub>2</sub> -64 pulp -71 FINAL READING AT -2.0	TiO <sub>2</sub> -45 pulp +30 FINAL READING AT -2.2
80	30.1	31.5	19	21	23	38	18
58	69	38	13	15.5	34	34	9
87.2	87.5	85.5	89.2	88.2	88.7	87.9	91.7
79.9	81.3	79.9	80.6	79.8	79.1	80.5	76.0
.38	.74	.58	.65	.71	.78	.74	.36
92	57.8	56.8	48.3	48.1	43.6	41.1	39.7

ALL SYSTEMS READINGS WERE EXPRESSED IN MILLIVOLTS

## Discussion of Results

The conductivity readings which are a measure of the total dissolved ionizable solids content, remained fairly constant in all the systems. This was due to the fact that all the systems were approximately in the same final SCD range of  $\pm 4$  mV, which is not a large enough SCD deviance to greatly change its conductivity reading. System # 6 had the highest conductivity reading of 80 mhos. This particular system took the greatest amount of time to stabilize because the response of the SCD was suppressed. This was due to the fact that as the solution's resistance decreases, a large fraction of the current is diverted in the annulus. Consequently, less signal is available to be collected at the electrodes.

In general the % transmission of the filtrate increased as the % retention increased. This was due to the fact that the pigments were more tightly packed or held onto the fibers, in the systems which had the higher % retentions, thereby forbidding the  $\text{TiO}_2$  particles to fall through the 100 mesh screen and into the filtrate.

Higher scattering coefficients of the  $\text{TiO}_2$  (.58 to .78), in most cases, were obtained in those systems producing the lower % retention levels. This means that these systems gave the best pigment distribution. The high retention systems gave somewhat lower (.40 to .66) scattering coefficients, thus indicating flocculation of the individual pigment particle to groups above .1 to .2 micron size which is the optimum size for opacifying papers.



The most curious part of this experimental data was that even though all the systems were run in approximately the same SCD range where maximum retention is to occur, there were wide variations in % retention (from 82.6 to 31.7%) in some individual systems.

Systems # 1, 2 ( $\text{TiO}_2$  highly negative and pulp highly positive) and system # 3 ( $\text{TiO}_2$  highly positive and pulp highly negative) had the highest % retentions. These initial starting conditions caused the pigments to become greatly attracted to the fibers. When adjusted to their final SCD readings, maximum agglomeration and flocculation also occurred. This is the condition needed for optimum retention to occur.

Most of the other systems with lower % retention were also at their maximum flocculation point. But consisting of weaker flocs than those of systems #1 - #3, thereby being disrupted by shear more easily, resulting in lower retention.

In the high retention systems the proper conditions were met for excellent bridging of one particle to another, to occur.

Each individual system has a certain plateau or measure of the absorption - neutralization characteristic. What may have happened was that the length of these plateaus were altered in such a way as to produce good retention in some systems but not in others. In the systems with low retention, steric hindrance, to a small degree, may have occurred to prevent complete absorption of the ionics of any kind and inhibit the agglomeration/flocculation process.

Although the diffuse layer is bound to the charged surface by electric forces, it is at least partially mobile--free to move

with the liquid phase. This motion is altered by electric forces acting on the liquid and the surface. Since different electric forces were initially applied to these various systems, this altered motion of the diffuse layer, also contributed to the variations of retention.

In system #7 and #11, the prerequisite conditions (low values on SCD) for flocculation to occur were initially met. But both these systems had poor retentions of 57.8% and 43.6%, respectively, because of the previously mentioned reasons. Although they both had the highest scattering coefficients of all the systems, which means these particular systems will provide the papermaker with the best distribution of  $\text{TiO}_2$ .

It was also found that all these systems are sensitive around the isoelectric point. The addition of a polyelectrolyte at this point, causes a much greater amount (in the order of 1.5 to 3 times) of equal strength and opposite charge polyelectrolyte to be added back into the system, in order to return the system to its isoelectric point.

The economic factors required to achieve these desired systems must also be considered. Even though system #1 had the highest  $\text{TiO}_2$  retention, it required the most chemical polymer addition (76 ml) to obtain its final SCD value. While systems 7 and 8, required only a few drops of polymer to reach their final SCD value, their retentions were approximately 25% lower than the #1 system. An economic compromise must be calculated, which is beyond the scope of this thesis, to determine the most feasible system.

Systems #1 and #2 had approximately the same initial charges on their  $\text{TiO}_2$  and pulp slurries. A .1% dispersing agent (Calgon T) was added to the  $\text{TiO}_2$  slurry in the #2 system, with no addition of it, in #1. Both systems produced similar test results, with system #1 giving a higher % transmission (86 vs 71) and % retention (82.6 vs 79.5). System #2 had the higher scattering coefficient (.66 vs .56) due to the fact that the dispersing agent produced better pigment distribution.

System #12 produced a low % retention (41.1) due to the fact that both the  $\text{TiO}_2$  and pulp slurries were initially at highly negatives values (-64 mV and -71 mV) which represented a condition characterized by strong dispersion and potential poor floccing and retention. According to theory, this condition should also have occurred if both slurries were initially highly positive, as was the case in system #5. Apparently it did not, for system #5 had a much greater retention of the  $\text{TiO}_2$  (70.4%) as compared to that of 41.1% retention for #12. No explanation for this occurrence can be given.

System #11 (both slurries at low negatives values) had approximately the same experimental results as the #12 system. Apparently it does not matter if both slurries are either at large or small initial negatives values because both will produce the same end results.

System #13 which simulates some normal papermaking systems (.05% cationic polyelectrolyte added to pulp/ $\text{TiO}_2$  slurry) used in the industry today, gave the poorest experimental results.

At this time it must be brought out that laboratory retention

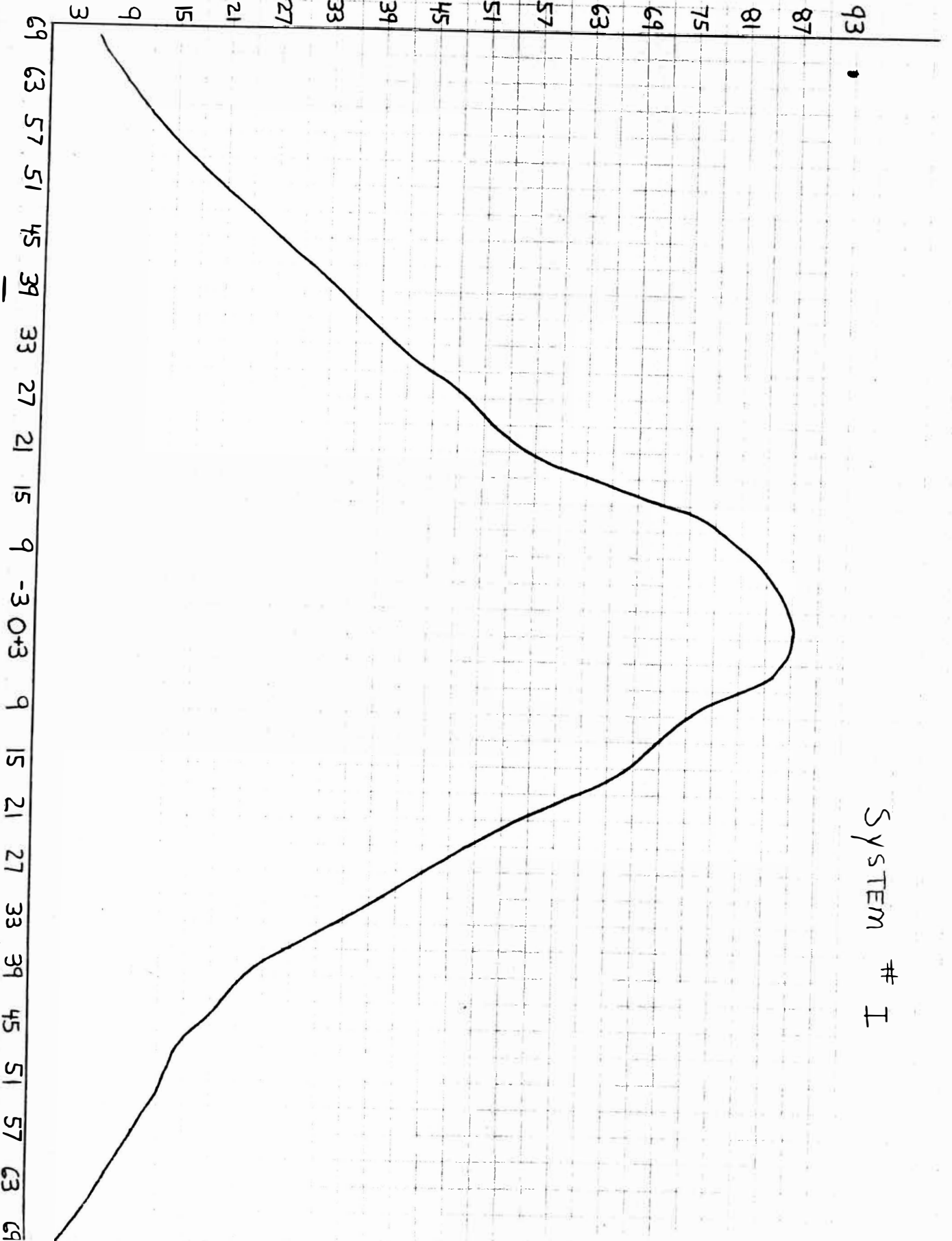
studies do not correlate closely with results obtained on commercial machines. This particular laboratory system (#13) must of had a great deal of experimental uncertainty to its otherwise normal performances in the mill.

## Graphs

A graph of the % light transmission of the filtrate versus millivolts on the SCD was made for system #1 (highest % retention -82.6) and system #13 (lowest % retention -39.7). Using the supposition that the maximum % light transmission correlates closely to the same area where maximum retention will also be found; system #13 provided further corroboration that maximum retention, depending on its initial SCD charges, does not always occur between -3mV and +3 mV. Here maximum % light transmission occurred at -29 mV, while system #1 had its maximum % light transmission at +2 mV.

System # I

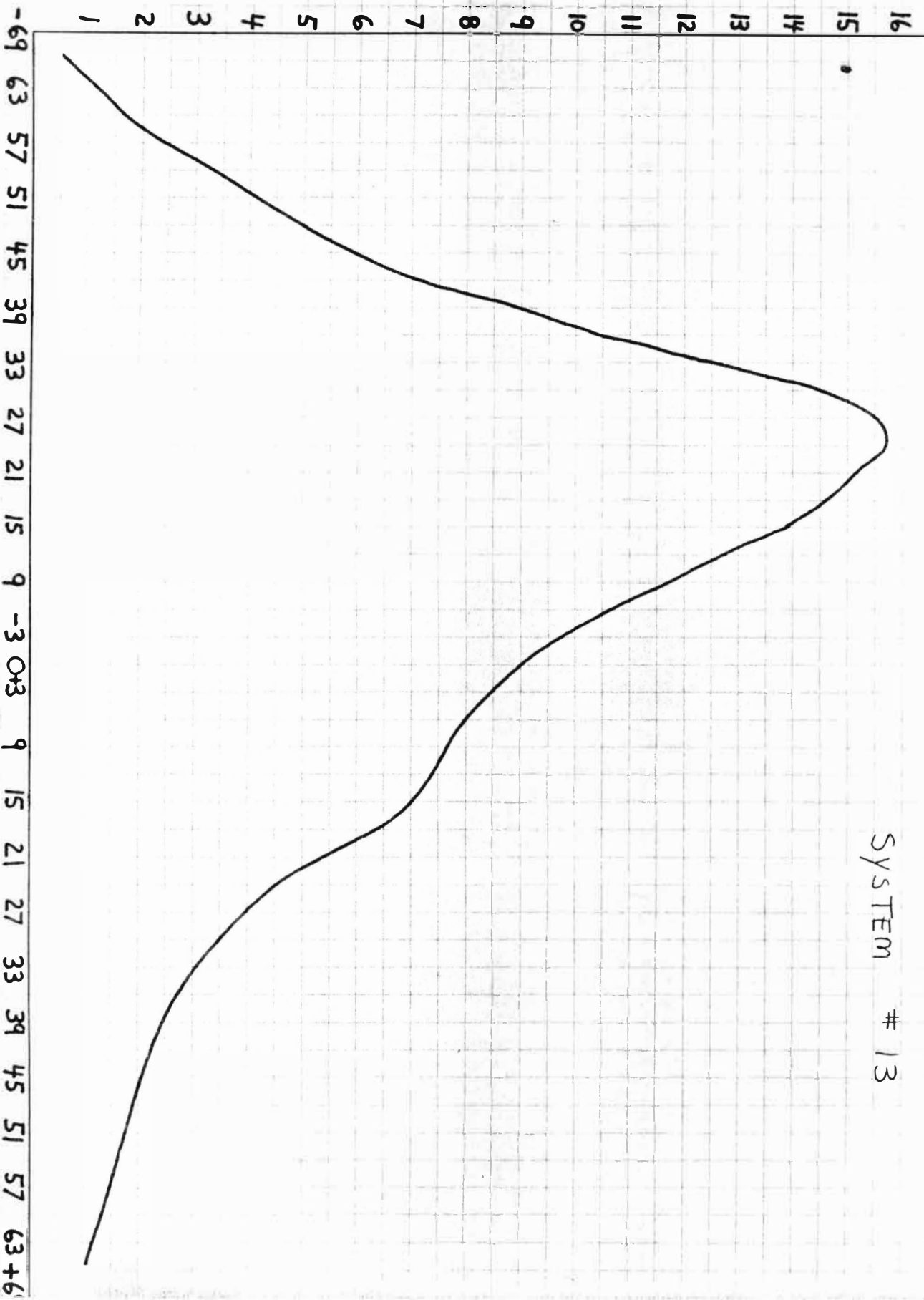
% TRANSMISSION



MILLIVOLTS ON SCD

% TRANSMISSION

SYSTEM # 13



MILLIVOLTS ON SCD

### Experimental Errors

1. From time to time there was drifting of the SCD needle.
2. It was recently proven that zeta potential may change with time.
3. A change in distilled water content may have contained a little more  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  ion which are available for absorption on the negatives particles. This in turn means that the cationic polyelectrolyte will have to compete with the already absorbed ions and therefore be less effective.



## Conclusions

Maximum  $\text{TiO}_2$  retention, depending on initial SCD values on the pulp and  $\text{TiO}_2$  slurries, will not always occur in the previously theorized electrokinetic range of  $\pm 3$  mV. The reasons for these variations in % retention, in the different systems, are that these different starting charges, either; alter the motion of the diffuse layer, change the motion of the diffuse layer, change the system's plateau, bring about steric hinderance, vary the degrees of flocculation strength, provide pigment attraction to the fibers and or provide pigment attraction to the fibers and or provide proper conditions for brigding to occur.

Systems obtaining the best retentions and overall results were those having high (appr. -60 mV) initial negative charges on the  $\text{TiO}_2$  slurry and high positive charges (appr. +60 mV) on the pulp and also on the system with these same charges reversed on the slurries.

The addition of a dispersing agent to an initially highly negative  $\text{TiO}_2$  slurry will produce similar end results of brightness, opacity, and % retention that of another system having the same starting conditions, with no addition. The dispersing agent will give a higher (18% increase) scattering coefficient.

These systems are sensitive around their isoelectric point. Since these observations were made on very minute systems as far as volume is concerned, it will be impossible to determine if this would also be the case in the commercial industry.

Economic factors required to achieve these desired systems must

be analyzed to determine the most feasible system. Can not just pick the system with the highest % retention, without comparing the amount of polyelectrolytes required to obtain this end result.

With the initial conditions of both slurries at either large negative (-60 mV) or at low negative (-4 mV) electrokinetic values, similar end results of brightness, opacity, % retention and scattering coefficient will be obtained from either system.

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