



Western Michigan University
ScholarWorks at WMU

Paper Engineering Senior Theses

Chemical and Paper Engineering

12-1970

The Effects of pH on Cationic Agents to Increase the Efficiency of TiO₂ in Paper

Stanley L. Oakleaf
Western Michigan University

Follow this and additional works at: <https://scholarworks.wmich.edu/engineer-senior-theses>



Part of the Wood Science and Pulp, Paper Technology Commons

Recommended Citation

Oakleaf, Stanley L., "The Effects of pH on Cationic Agents to Increase the Efficiency of TiO₂ in Paper" (1970). *Paper Engineering Senior Theses*. 413.
<https://scholarworks.wmich.edu/engineer-senior-theses/413>

This Dissertation/Thesis is brought to you for free and open access by the Chemical and Paper Engineering at ScholarWorks at WMU. It has been accepted for inclusion in Paper Engineering Senior Theses by an authorized administrator of ScholarWorks at WMU. For more information, please contact wmu-scholarworks@wmich.edu.



THE EFFECTS OF pH
ON CATIONIC AGENTS TO
INCREASE THE EFFICIENCY
OF TiO_2 IN PAPER

Submitted to Dr. Stephen
Kukulich in fulfillment of
Senior Thesis course 471.

Stanley L. Oakleaf
Winter term of 1970

ABSTRACT

The effect of pH on the efficiency of the cationic agents, Kymene 557 (Epichlorohydrin) and Tydex (Polyethylenimine), was studied, and the efficiencies of the two cationic agents were compared.

The pH at which cationic agents are most effective, considering percent retention of titanium dioxide, is pH 5.7 at the time of titanium dioxide slurry addition. The pH for optimum opacity in a sheet is pH 6.0.

A pH that is controlled by alum, rather than independently of alum, produces higher titanium dioxide retentions and opacities. Maximum efficiency is not controlled by pH alone. An alum loading of about 3.5% should be present at the time of titanium dioxide addition.

Although the pH 5.7 produces the best results at the point just before the titanium dioxide-cationic agent slurry is added, if one retains this pH, by adjusting pH of dilution water, right up to the point of sheet formation, the efficiency of the cationic agent decreases.

Comparing Kymene and Tydex as cationic agents, Kymene produced the best retention of titanium dioxide and opacity in the sheet, when the cationic agent was added to the titanium dioxide slurry before addition to the pulp slurry. The superiority of Kymene can be predicted by the higher magnitude of positive zeta potential it produces on the titanium dioxide particles. At pH 7.0 Kymene produced a zeta potential of +2.54mV on the titanium dioxide, and Tydex only produced +0.99mV.

TABLE OF CONTENTS

LITERATURE SURVEY	1
EXPERIMENTAL DESIGN	8
DISCUSSION OF RESULTS	11
CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK	14
APPENDIX	I
SAMPLE CALCULATIONS	II
ZETA POTENTIAL RESULTS	IV
RESULT DATA SHEETS	V
EXPLANATION OF GRAPH SYMBOLS	XIII
GRAPHICAL ANALYSIS OF RESULTS	XIV
BIBLIOGRAPHY	XXII

LITERATURE SURVEY

In recent years the use of retention aids for titanium dioxide has increased substantially with the introduction of synthetic organic retention aids such as cationic, non-ionic, and anionic polymers. These retention aids have great possibilities for increased retention. They are specifically designed, and present no BOD problems. (1)

The theory motivating the development of cationic retention aids was based on the well known physical property that if the electrokinetic potentials of the two materials have the same sign they repel each other. Thode and Htoo (2) determined that when cellulose fibers are dispersed in water they have a highly negative potential, the sign of which is extremely difficult to reverse. Most fibers are also anionic although their potential is not considered to be as strong. Therefore, if one disperses some cations, in a filter solution, which will adhere to the surface of the filler and change the surface charge, then a "chemical bridge" (3) can be formed between the filler and cellulose fiber of like charge to improve the retention.

The cationic retention aids such as Nalco 600-D1593 look very promising as retention aids that bond through electrokinetic attraction. (4) But, there are still many uncertain aspects about these aids, such as: best point of addition; ideal pH; effect of various amounts of rosin size; ideal aluminum ion concentration; and best headbox temperatures. (4)

Laboratory work with polyacrylamide in paper machine furnishes shows the performance of this polymer to be greatly affected by the alum loading and the pH. Within alum loading of 2-3% on the fiber, a pH around 6 is desirable. With higher alum loadings the maximum effect takes place at a high pH. (5) There is a maximum amount of alum beyond which any further increase, regardless of the pH, is detrimental. (6) Also, any pH adjustment of the furnish containing the filler must be done before the dilute polymer solution is added. (7)

The polymer and alum appear to attach the pigment particles to the fiber surface by a chemical linkage.

The nature of this linkage has not been described but it probably involves a coordination with aluminum and olation in a manner similar to that of rosin sizing.(5)

The following discussion concerning the effects of pH on retention were not observed in the presence of a cationic retention aid, but possibly similar events will occur when a cationic aid is present.

Alum is most generally used in paper mills to control pH. The amount of alum used by papermakers has been considered an important factor regarding filler retention. In terms of dry alum based on weight of fiber, Willets (8) reported 3% to be optimum for titanium dioxide, and Haslam and Steele (9) reported the same amount for highest zinc sulfide retention. Brill (10), however, found 1 to 2 % alum gave maximum titanium dioxide retention.

Since pH of the papermaking system has been considered a factor in filler retention, the possibility that discrepancies between reported optimum alum concentrations may have been associated with the pH at the time of filler addition. Differences in the water used by the various investigators possibly could have resulted in the same optimum pH but at different alum concentrations. (6)

Fraik (6) checked this theory by producing pH conditions independent of those caused by alum. Sodium hydroxide or sulfuric acid was added to pigmented furnishes containing alum in a range of 0 to 5%. The water used to dilute each furnish at the sheet mold was adjusted by the same means to the same pH as the test furnish. His results indicated that pH adjustment after alum and filler addition does affect retention since the position of the retention curves shift up or down with changes in pH. The maximum retention occurred at a pH between 5 and 6. (6)

To further evaluate the effect of pH at the time of filler addition, sodium hydroxide or sulfuric acid was introduced to aliquot parts of beaten pulp containing different amounts of alum prior to the addition of filler to create pH conditions differing from those caused by the alum. Again the pH of the dilution water was adjusted to match the furnish to be tested. By this method it was found that the relationship between percent alum and retention no longer exists. (6) However, a relation was found between retention and pH encountered at the time of the filler addition to the system. It was again found that

maximum retention occurred in the 5 to 6 pH range.

From this observation it would appear that the effect of alum depends on the pH it produces. (6)

Considering possible changes of charge on pulp or filler encountered with variation in pH, it appears that differences in the electrokinetic properties of these two materials may be the most significant in retention of titanium dioxide.

The electrokinetic properties of cellulose have been studied by many people. Thode and Htoo (2) indicated that both sized and unsized pulps originally assume a negative charge in water. As Thode and Htoo added increasing amounts of alum to pulp suspensions, the strength of the charge was decreased until an isoelectric point was reached at approximately pH 4.7. Mysels (11) states that the electrokinetic charge on the fiber is reversed when the pH decreases below the isoelectric point.

Fraik (6) completed a study in which a similar change of charge was observed on titanium dioxide by determining the electrophoretic mobility of pigment in suspensions, which were adjusted to a range of pH values with alum. However, the titanium dioxide isoelectric point was found to occur at 5.2. In Fraik's

retention experiments, maximum retention was always obtained when the pH at the time of the filler addition was near 5.2. (6) Since maximum flocculation of a material can be expected at its isoelectric point, it appears that a major part of the retention phenomena is related to flocculation of the filler used. (6)

Thus in Fraik's work, the possible influence of charge attraction seems to be negligible. According to the charge attraction theory, maximum retention would be expected at about pH 4.95, not at pH 5.2 as he observed. This value of 4.95 represents the pH at which the maximum difference in charge would be encountered since the pigment would be positively charged in the presence of a negatively charged fiber. However, both charges would be of small magnitude. (6)

Even though the the isoelectric point of the titanium dioxide, observed by Fraik (6), occurs at a different pH than Thodes and Htoo's (2) reported value for wood pulp, the possibility of coflocculation cannot be overlooked. In the case of titanium dioxide used throughout Fraik's work, flocculation was observed in the 5.5 to 5.5 pH range. (6) Since the charge of the pigment should be weak at the pH reported to be the isoelectric point of pulp, the re-

pulling force between the two materials may be sufficiently weak to allow the formation of a common floc. (6)

EXPERIMENTAL DESIGN

In this paper there will be a comparison of Tydex (Polyethylenimine) and Kymene (Epichlorohydrin) used as cationic agents for the retention of titanium dioxide. The following solutions were made: 5% titanium dioxide solution; 5% titanium dioxide solution plus 2% Kymene (based on weight of titanium dioxide); and 5% titanium dioxide solution plus 2% Tydex (based on weight of titanium dioxide). The solutions were checked for zeta potential by the electrophoresis method. The values obtained indicate the potential these cationic agents have for changing the charge on the titanium dioxide particles.

To test the efficiency of the cationic agents at varying pH values, conditions were kept as constant as possible. Ten percent titanium dioxide, based on the weight of pulp, containing 2% cationic agent (cationic agent/TiO₂) was used for experimental runs C thru I. Ten percent titanium dioxide was used because it is a large enough quantity that variations in the amount of titanium dioxide retained at various pH values can be easily recognized. Two percent cationic agent was used because a previous thesis by Neil Hartman on cationic agents showed the best retention with 1.5% to 2% cationic agent based on the weight of the titanium dioxide.

The effectiveness of the cationic agents is measured by the retention of titanium dioxide, the opacity of the sheet, and the scattering coefficient of the titanium dioxide, found by using the Judd chart of the Kubelka-Munk equation.

In experimental runs C and D (C using Kymene and D

using Tydex) the pH was controlled exclusively by alum, and the pH of the water used. The results were studied in the following way: By plotting percent titanium dioxide retention versus pH at time of titanium addition; by plotting titanium dioxide scattering coefficient versus pH; and by plotting TAPPI opacity versus pH.

For experimental runs E, F, G, and H, Kymene was used for all four runs, because it seemed to be more effective than Tydex. The pH was controlled independently from the alum by using sodium hydroxide and sulfuric acid to control pH. This way one can find out if the alum just affects retention due to the pH it produces. These results were studied by the following graphs: Scattering coefficient of titanium dioxide versus pH held constant through production of the handsheet; percent opacity versus pH; and retention of titanium dioxide versus both pH and percent alum.

Experimental runs I and J were exactly like runs C and D except that the pH at the time of sheet formation was adjusted to 5.5, which seemed to be the pH which was most efficient at the time of filler addition. These runs were evaluated with graphs similar to those used for C and D.

Experimental runs A and B (using Kymene and Tydex respectively) were quite different from the other runs. Runs A and B were a test to see if the cationic agent could cause a reversal of charge on the pulp fibers before the titanium dioxide is added. Two percent cationic agent based on the weight of the pulp was added to the pulp slurry after

the alum and before the titanium dioxide. The runs were evaluated just like runs C and D.

The pulp used for all handsheets was bleached softwood sulfite. It was refined in a Valley beater to a CSF of 430. Handsheets were made in the Noble and Wood handsheet mold (TAPPI standard T-205 m-58).

The titanium dioxide was dispersed in an epinbach mixer at 5% solids. The cationic agents were added dropwise, at 10% solids, as the mixer ran.

The handsheets were conditioned and weighed (TAPPI T-404 m-49). They were tested for: Opacity (TAPPI T-452); brightness (TAPPI T-402 m-49); scattering coefficient of fiber; scattering coefficient of titanium dioxide; Sx; % ash (T-413); percent titanium dioxide; percent retention of titanium dioxide; and basis weight.

See appendix for graphical results mentioned above.

DISCUSSION OF RESULTS

1. Results with pH controlled by alum concentration prior to titanium dioxide addition (Runs A,B,C,D,I,& J on pages XIV thru XVII in the appendix):

At the time of the titanium dioxide addition to the pulp and alum slurry, the pH which averages out to be the most effective for retention of titanium dioxide, for all cases in which pH is controlled by alum, is about pH 5.7, or at about 3.5% alum addition.

The most effective pH for percent TAPPI opacity in these runs was around pH 6.0. This higher pH for optimum percent opacity could be due to a little better dispersion of the titanium dioxide at pH 6.0, which can be observed through the optimum scattering coefficient of the titanium dioxide occurring at a higher pH than the pH for optimum titanium dioxide retention.

Considering the four runs (C,D,I,J) in which the cationic agent was mixed into the titanium dioxide slurry before addition to the pulp, Kymene was superior to Tydex in both percent retention of titanium dioxide and percent opacity in the handsheets. In runs C and D where the pH was not adjusted just prior to sheet formation, the optimum retention of titanium was 69%, and the opacity was 89% with Kymene, compared to 52% and 87% respectively with Tydex added to the titanium dioxide slurry. Comparing runs I and J where the pH was adjusted at sheet formation to pH 5.5, the optimum retention of titanium dioxide was 59%, and the opacity was 87%

with Kymene, compared to 42% and 34% respectively with Tydex added. Tydex used in run J produced extremely poor results. The results indicate that forming the sheet at the pH 5.5 possibly caused the zeta potential of the titanium dioxide slurry to revert back to a negative value.

This superiority of kymene is basically due to the higher positive zeta potential that Kymene produces on the titanium dioxide particles. Kymene in a titanium dioxide slurry produces a zeta potential of +2.42mV, and Tydex only produces a zeta potential of +0.99mV (page IV of appendix).

The only case in which Tydex showed superiority over Kymene was when 2% cationic agent, based on the weight of the pulp, was added to the pulp, rather than to the titanium dioxide slurry (runs A & B, page XIV of appendix). But this method must be ruled out as an efficient way to retain titanium dioxide, because it did not retain any more titanium dioxide than the Kymene added to the titanium slurry. Also it is a more expensive method because the 2% Tydex is based on the pulp weight rather than the titanium dioxide weight which is much less.

2. Results with pH controlled independently of alum, using sodium hydroxide and sulfuric acid, and the pH is kept constant through the whole cycle of sheet formation (Runs E, F, G, & H, pages XVIII thru XXI of appendix):

This experiment indicated that one can obtain a percent titanium dioxide retention versus pH curve by controlling pH independently of the percent alum, which is very similar

to the percent titanium dioxide retention curve obtained when pH is controlled by percent alum present. The most efficient independently obtained pH was 6.0 which is relatively close to the optimum alum obtained pH of 5.7. But on the other hand the highest titanium dioxide retentions were obtained on the 2% and 4% alum runs of the independently obtained pH experiments, and the alum loading of 3.5% gave the optimum retention in the alum controlled pH experiments. Therefore the proper amount of alum as well as the proper pH produces the best titanium dioxide retention.

CONSLUSIONS AND SUGGESTIONS FOR FURTHER WORK

The pH at which cationic agents are most effective, considering percent retention of titanium dioxide, is pH 5.7 at the time of titanium dioxide slurry addition. The pH for optimum opacity in a sheet is pH 6.0.

A pH that is controlled by alum, rather than independently of alum produces higher titanium dioxide retentions and opacities. Maximum efficiency is not controlled by pH alone. An alum loading of about 3.5% should be present at time of titanium dioxide addition.

Although the pH 5.7 produces the best results at the point just before the titanium dioxide slurry is added, if one retains this pH by adjusting the pH just before sheet formation, the efficiency of the cationic agent decreases.

Comparing Kymene (Epichlorohydrin) and Tydex (Polyethyleneimine), the cationic agent Kymene produced the best retention of titanium dioxide and opacity in the sheet. This is easily understood by observing the zeta potentials which these agents produce on titanium dioxide particles, by adhering to the outer perimeter of the particles. Bleached sodium sulfite softwood pulp has a zeta potential of -5.2 mV, and a titanium dioxide slurry with nothing added has a zeta potential of -2.67 mV. These will repel one another, so a cationic agent is added to the titanium dioxide slurry to produce a positive charge. Kymene produces a zeta potential of +2.42 mV on the titanium dioxide, but Tydex only produces +0.99 mV on the

titanium dioxide. Therefore it is logical that the Kymene-titanium dioxide slurry would be attracted more to the pulp.

Of course zeta potentials do change somewhat as pH varies, and the charge attraction is not the only thing that causes titanium dioxide retention. As the pH decreases, one approaches the isoelectric point of both the titanium dioxide and the pulp, therefore flocculation increases. So at the optimum pH of 5.7, the maximum retention is probably created through the right combination of chemical bonding and coflocculation.

Further work could be done in this area of study. More study should be done on the effect of pH on zeta potential produced by cationic agents. Also more work could be done on comparing other cationic agents with Kymene.

APPENDIX

SAMPLE CALCULATIONS

1. For experimental runs A and B:

17.5g Pulp (940ml of pulp slurry at 1.86% consistency)
 2.0g Titanium Dioxide (4.0ml of 5% TiO_2 solution)
 0.4g Cationic Agent (4.0ml of 10% active solution)

This produces 10% TiO_2 and 2% cationic agent in the weight of a handsheet.

2. For all other experimental runs a titanium dioxide slurry was made before addition to pulp slurry:

20.0g Titanium dioxide
 376.0g Water
 0.4g Cationic agent (4.0ml of 10% active solution)

This produces: 5% TiO_2 and 2% cationic agent/ TiO_2 .

3. Pulp:

8"x8" Handsheets, 6% moisture
 Sheet weight = 2.88g
 Basis weight = 43.0lbs./24x36-500 ream
 Brightness = 74.5
 Opacity = 79.5
 Corrected
 Opacity (37#) = 75.3 (Using Judd Chart).
 Corrected SX = 1.81
 S = .0489 = (1.81/37.0)
 % Ash = .37% = (.0058g OD ash/1.5652g OD fiber)

4. Titanium Dioxide filled handsheet:

8"x8" Handsheets, 6% moisture
 Sheet weight = 2.73g
 Basis weight = 40.7lbs./24x36-500 ream
 Brightness = 79.1
 Opacity = 91.0
 Corrected
 Opacity (37#) = 88.9 (Using Judd Chart)
 % Ash = 7.52% = (.0996g OD ash/1.3248g OD fiber)
 % Ash (due to 5% Alum) = 0.65%
 % Ash (due to fiber) = 0.37%
 % Titanium Dioxide = 6.50% = (7.52% - 0.65% - 0.37%)
 Corrected SX (37#) = 3.46
 S of TiO_2 = 0.74 = $\frac{(3.46/37.0 - 0.9350(.0489))}{0.0650}$
 % addition TiO_2 = 10.0%
 % retention TiO_2 = 65.0% = (6.50%/10.0%)

5. Correcting Opacity to a 37.0 lbs/24x36-500 ream:

Initial Basis Wt.	= 40.7 lbs/24x36-500 ream
Uncorrected Opacity	= 91.0
Brightness	= 79.1
Uncorrected SX	= 3.30 (Judd Chart)
Corrected SX	= 3.46 $= (37.0/40.7) \times 3.80$
Corrected Opacity	= 88.9 (Judd Chart)

EFFECT OF CATIONIC AGENTS ON ZETA POTENTIAL

Solution	Zeta Potential (at pH 7.0)				AVG.
	Run 1	Run 2	Run 3	Run 4	
1. 5% TiO ₂	-2.54	-2.55	-2.41	-3.20	-2.67mV
2. 5% TiO ₂ plus 2% Tydex on weight of TiO ₂	+0.83	+1.20	+0.94	+0.95	+0.99mV
3. 5% TiO ₂ plus 2% Kymene on weight of TiO ₂	+2.39	+2.40	+2.26	+2.63	+2.42mV

Sample Calculation: (Run 1 of 5% TiO₂ solution)

$$\zeta = \frac{4\pi\eta V}{HD}$$

ζ = zeta potential (mV)

V = particle velocity (m /sec.)

H = potential gradient (volts/cm)

η = viscosity (poises)

D = dielectric constant

$$\zeta = \frac{4 (3.14) (1 \times 10^{-2}) (1.16 \times 10^{-3})}{(7.16) (80)} \times 10^7 = -2.54 \text{ mV}$$

↑
Sign comes from
direction of move-
ment in cell.

DATA SHEETS

10% TiO₂ and 2% Kymene based on pulp weight are added separately to the pulp slurry, rather than in a TiO₂-Kymene slurry.

Sample	% Alum	% TiO ₂	% Kymene	pH after alum add.	pH after TiO ₂ add.	pH at.sht. formation	Bright.	uncorr. B.W.
0-A	0	0	0	8.2	8.2	8.3	74.5	43.0
1-A	0	10	0	8.2	8.2	8.3	77.0	41.0
2-A	0	10	2	8.1	8.1	8.3	72.7	42.0
3-A	1	10	2	7.1	7.3	8.1	77.9	39.5
4-A	2	10	2	6.6	6.8	7.9	79.8	41.6
5-A	3	10	2	6.0	6.1	7.9	79.1	39.2
6-A	4	10	2	5.2	5.4	7.8	79.6	41.3
7-A	5	10	2	4.8	4.9	7.8	79.7	40.4
8-A	6	10	2	4.6	4.7	7.7	76.4	40.4
9-A	7	10	2	4.5	4.7	7.7	75.9	40.3

Sample	uncorr. opacity	corr. opacity	uncorr. SX	corr. SX	% ash	% TiO ₂	% TiO retention	S TiO ₂
0-A	79.5	75.3	2.10	1.81	.37	--	---	--
1-A	80.4	77.8	2.25	2.03	2.04	1.67	16.7	.41
2-A	86.5	84.2	2.67	2.45	3.89	3.52	35.2	.54
3-A	89.2	87.8	3.40	3.18	5.83	5.33	53.3	.74
4-A	89.3	87.2	3.58	3.18	6.22	5.59	55.9	.72
5-A	89.6	88.3	3.55	3.35	6.68	5.92	59.2	.75
6-A	90.1	88.0	3.68	3.30	7.02	6.13	61.3	.71
7-A	88.7	86.9	3.40	3.12	6.02	5.00	50.0	.76
8-A	88.4	86.7	3.18	2.92	5.54	4.39	43.9	.74
9-A	87.7	85.8	3.00	2.75	5.00	3.72	37.2	.73

DATA SHEETS

10% TiO_2 and 2% Tydes based on pulp weight are added separately to the pulp slurry, rather than in a TiO_2 -Tydex slurry.

<u>Sample</u>	<u>% Alum</u>	<u>% TiO_2</u>	<u>% Tydex</u>	<u>pH after alum add.</u>	<u>pH after TiO_2 add.</u>	<u>pH at sht. formation</u>	<u>uncorr. opacity</u>	<u>corr. opacity</u>
2-B	0	10	2	8.1	8.1	8.0	89.3	88.0
3-B	1	10	2	7.1	7.7	7.9	89.9	88.3
4-B	2	10	2	6.4	7.0	8.0	90.7	89.1
5-B	3	10	2	6.1	6.5	8.0	90.5	88.2
6-B	4	10	2	5.3	6.2	8.1	90.0	88.0
7-B	5	10	2	4.9	5.8	8.2	89.0	87.0
8-B	6	10	2	4.6	4.7	8.1	85.3	85.3

<u>Sample</u>	<u>Bright.</u>	<u>uncorr. B.W.</u>	<u>uncorr. SX</u>	<u>corr. SX</u>	<u>% ash</u>	<u>% TiO_2</u>	<u>% TiO_2 retent.</u>	<u>% TiO_2</u>
2-B	71.5	39.2	2.96	2.80	6.30	5.93	59.3	.50
3-B	73.6	39.8	3.17	2.95	7.00	6.50	65.0	.52
4-B	76.5	39.4	3.50	3.28	7.46	6.83	68.3	.65
5-B	76.7	40.7	3.51	3.19	7.26	6.50	65.0	.63
6-B	74.9	40.4	3.30	3.02	7.19	6.30	63.0	.57
7-B	74.1	40.7	3.10	2.82	6.71	5.69	56.9	.53
8-B	74.7	37.0	2.65	2.65	5.66	4.51	45.1	.55

DATA SHEETS

Slurry of 10% TiO_2 and 2% Kymene (Kymene/ TiO_2) added to pulp slurry.

<u>Sample</u>	<u>% Alum</u>	<u>% TiO_2</u>	<u>% Kymene</u>	<u>pH after alum add.</u>	<u>pH after TiO_2 add.</u>	<u>pH at sht. formation</u>	<u>uncorr. opacity</u>	<u>corr. opacity</u>
1-C	0	10	2	8.2	8.2	8.2	90.1	88.0
2-C	1	10	2	7.2	7.3	8.3	88.8	88.8
3-C	2	10	2	6.7	6.8	8.0	91.5	89.1
4-C	3	10	2	6.2	6.3	8.0	91.5	89.3
5-C	4	10	2	5.2	5.3	7.7	90.7	89.0
6-C	5	10	2	4.7	4.8	7.7	91.0	88.9
7-C	6	10	2	4.6	4.7	7.7	89.6	87.9

<u>Sample</u>	<u>Bright.</u>	<u>uncorr. B.W.</u>	<u>uncorr. SX</u>	<u>corr. SX</u>	<u>% ash</u>	<u>% TiO_2</u>	<u>% TiO_2 retent</u>	<u>S TiO_2</u>
1-C	77.7	41.0	3.52	3.18	6.45	6.08	60.8	.66
2-C	79.3	37.0	3.40	3.40	6.61	6.11	61.1	.75
3-C	77.0	41.7	3.73	3.31	7.39	6.76	67.6	.65
4-C	79.9	41.6	4.00	3.55	7.68	6.92	69.2	.74
5-C	80.2	39.9	3.83	3.55	7.69	6.80	68.0	.76
6-C	79.1	40.7	3.80	3.46	7.52	6.50	65.0	.74
7-C	79.1	40.1	3.55	3.28	6.41	5.26	52.6	.82

DATA SHEETS

Slurry of 10% TiO₂ and 2% Tydex (Tydex/TiO₂) added to pulp slurry.

<u>Sample</u>	<u>% Alum</u>	<u>% TiO₂</u>	<u>% Tydex</u>	<u>pH after alum add.</u>	<u>pH after TiO₂ add.</u>	<u>pH at sht. formation</u>	<u>uncorr. opacity</u>	<u>corr. opacity</u>
1-D	0	10	2	8.2	8.2	8.2	90.8	87.4
2-D	1	10	2	7.5	7.6	8.0	86.7	84.6
3-D	2	10	2	7.0	7.3	7.9	87.1	86.8
4-D	3	10	2	6.3	6.4	7.9	86.5	86.8
5-D	4	10	2	5.2	5.4	7.8	88.7	86.6
6-D	5	10	2	4.7	4.8	7.8	87.9	86.3
7-D	6	10	2	4.7	4.8	7.8	86.5	84.3

<u>Sample</u>	<u>Bright.</u>	<u>uncorr. B.W.</u>	<u>uncorr. SX</u>	<u>corr. SX</u>	<u>% ash</u>	<u>% TiO₂</u>	<u>% TiO₂ retent</u>	<u>S TiO₂</u>
1-D	76.5	43.4	3.55	3.03	4.68	4.31	43.1	.82
2-D	77.8	40.7	2.98	2.71	4.79	4.29	42.9	.62
3-D	77.8	39.6	3.22	3.01	4.97	4.34	43.4	.80
4-D	78.7	37.0	3.00	3.00	5.38	4.62	46.2	.75
5-D	80.3	41.0	3.48	3.14	6.05	5.16	51.6	.75
6-D	79.1	41.5	3.41	3.04	5.08	4.06	40.6	.87
7-D	78.1	41.1	3.00	2.70	4.66	3.51	35.1	.74

DATA SHEETS

Effect of Alum with pH controlled independently of the Alum.

Sample	% Alum	% TiO_2	% Kymene	pH after alum add.	pH after TiO_2 add.	pH at sht. formation	uncorr. opacity	corr. opacity
1-E	0	10	2	7.0	7.0	7.0	87.6	84.8
2-E	0	10	2	6.0	6.0	6.0	86.7	85.6
3-E	0	10	2	5.0	5.0	5.0	81.0	79.7
4-E	0	10	2	4.0	4.0	4.0	87.1	85.9

Sample	Bright.	uncorr. B.W.	uncorr. SX	corr. SX	% ash	% TiO_2	% TiO_2 retent	S TiO_2
1-E	78.7	42.3	3.18	2.78	5.08	4.71	47.1	.61
2-E	74.6	38.8	2.80	2.67	5.25	4.88	48.8	.53
3-E	78.0	39.3	2.35	2.22	3.64	3.27	32.7	.39
4-E	76.8	38.8	2.98	2.83	4.96	4.59	45.9	.44

Sample	% Alum	% TiO_2	% Kymene	pH after alum add.	pH after TiO_2 add.	pH at sht. formation	uncorr. opacity	corr. opacity
1-F	2	10	2	7.0	7.0	7.0	88.5	86.3
2-F	2	10	2	6.0	6.0	6.0	88.0	86.2
3-F	2	10	2	5.0	5.0	5.0	86.1	86.3
4-F	2	10	2	4.0	4.0	4.0	84.0	84.2

Sample	Bright.	uncorr. B.W.	uncorr. SX	corr. SX	% ash	% TiO_2	% TiO_2 retent	S TiO_2
1-F	78.6	41.0	3.32	3.00	5.83	5.20	52.0	.67
2-F	80.6	40.7	3.40	3.09	6.08	5.45	54.5	.68
3-F	81.8	36.6	3.15	3.19	5.97	5.34	53.4	.75
4-F	81.2	36.6	2.82	2.85	3.80	3.17	31.7	.93

DATA SHEETS

Effect of Alum with pH controlled independently of the Alum.

<u>Sample</u>	<u>% Alum</u>	<u>% TiO₂</u>	<u>% Kymene</u>	<u>pH after alum add.</u>	<u>pH after TiO₂ add.</u>	<u>pH at sht. formation</u>	<u>uncorr. opacity</u>	<u>corr. opacity</u>
1-G	4	10	2	7.0	7.0	7.0	87.3	87.1
2-G	4	10	2	6.0	6.0	6.0	87.5	86.5
3-G	4	10	2	5.0	5.0	5.0	85.8	85.1
4-G	4	10	2	4.0	4.0	4.0	79.8	79.4

<u>Sample</u>	<u>Bright.</u>	<u>uncorr. B.W.</u>	<u>uncorr. Sx</u>	<u>corr. Sx</u>	<u>% ash</u>	<u>% TiO₂</u>	<u>% TiO₂ retent</u>	<u>S TiO₂</u>
1-G	80.2	37.4	3.25	3.21	6.14	5.25	52.5	.77
2-G	80.3	38.5	3.26	3.14	5.82	4.93	49.3	.78
3-G	81.8	38.6	3.10	2.98	4.22	3.33	33.3	1.00
4-G	80.5	37.4	2.30	2.28	2.26	1.37	13.7	.99

<u>Sample</u>	<u>% Alum</u>	<u>% TiO₂</u>	<u>% Kymene</u>	<u>pH after alum add.</u>	<u>pH after TiO₂ add.</u>	<u>pH at sht. formation</u>	<u>uncorr. opacity</u>	<u>corr. opacity</u>
1-H	6	10	2	7.0	7.0	7.0	36.8	85.7
2-H	6	10	2	6.0	6.0	6.0	86.3	85.6
3-H	6	10	2	5.0	5.0	5.0	84.4	83.4
4-H	6	10	2	4.0	4.0	4.0	82.1	80.9

<u>Sample</u>	<u>Bright.</u>	<u>uncorr. B.W.</u>	<u>uncorr. Sx</u>	<u>corr. Sx</u>	<u>% ash</u>	<u>% TiO₂</u>	<u>% TiO₂ retent</u>	<u>S TiO₂</u>
1-H	81.6	38.8	3.22	3.07	5.66	4.51	45.1	.81
2-H	81.7	37.9	3.12	3.05	5.78	4.63	46.3	.77
3-H	80.8	38.9	2.85	2.71	4.42	3.27	32.7	.80
4-H	81.3	39.1	2.58	2.44	2.90	1.85	18.5	.98

DATA SHEETS

Slurry of 10% TiO_2 and 2% Kymene (Kymene/ TiO_2) added to pulp slurry, and pH is adjusted to 5.5 at sheet formation.

<u>Sample</u>	<u>% Alum</u>	<u>% TiO_2</u>	<u>% Kymene</u>	<u>pH after alum add.</u>	<u>pH after TiO_2 add.</u>	<u>pH at sht. formation</u>	<u>uncorr. opacity</u>	<u>corr. opacity</u>
1-I	0	10	2	8.0	8.0	5.5	87.3	85.4
2-I	1	10	2	7.0	7.1	5.5	86.4	85.8
3-I	2	10	2	6.6	6.6	5.5	87.7	86.0
4-I	3	10	2	6.0	6.1	5.5	88.7	87.2
5-I	4	10	2	4.9	5.0	5.5	88.7	86.7
6-I	5	10	2	4.5	4.6	5.5	87.7	86.0
7-I	6	10	2	4.3	4.4	5.5	85.5	82.5

<u>Sample</u>	<u>Bright.</u>	<u>uncorr. B.W.</u>	<u>uncorr. SX</u>	<u>corr. SX</u>	<u>% ash</u>	<u>% TiO_2</u>	<u>% TiO_2 retent</u>	<u>S TiO_2</u>
1-I	76.5	39.6	2.96	2.76	5.49	5.12	51.2	.54
2-I	80.0	38.5	3.10	2.98	5.39	4.89	48.9	.69
3-I	80.9	39.9	3.32	3.08	5.92	5.29	52.9	.70
4-I	80.7	39.9	3.50	3.24	6.61	5.85	58.5	.71
5-I	83.4	41.0	3.70	3.34	6.51	5.62	56.2	.78
6-I	81.2	42.0	3.35	2.95	5.52	4.50	45.0	.74
7-I	81.4	42.5	3.02	2.63	4.38	3.23	32.3	.74

DATA SHEETS

Slurry of 10% TiO_2 and 2% Tydex (Tydex/ TiO_2) added to pulp slurry, and pH is adjusted to 5.5 at sheet formation.

<u>Sample</u>	<u>% Alum</u>	<u>% TiO_2</u>	<u>% Tydex</u>	<u>pH after alum add.</u>	<u>pH after TiO_2 add.</u>	<u>pH at sht. formation</u>	<u>uncorr. opacity</u>	<u>corr. opacity</u>
1-J	0	10	2	8.0	8.0	5.5	87.2	83.8
2-J	1	10	2	7.1	7.2	5.5	86.7	83.4
3-J	2	10	2	6.6	6.7	5.5	87.4	83.6
4-J	3	10	2	5.8	5.9	5.5	86.2	83.8
5-J	4	10	2	4.8	4.9	5.5	86.1	82.9
6-J	5	10	2	4.5	4.6	5.5	84.9	82.0
7-J	6	10	2	4.3	4.4	5.5	85.7	82.0

<u>Sample</u>	<u>Bright.</u>	<u>uncorr. B.W.</u>	<u>uncorr. 3X</u>	<u>corr. 5X</u>	<u>% ash</u>	<u>% TiO_2</u>	<u>% TiO_2 retent</u>	<u>S TiO_2</u>
1-J	78.1	43.1	3.10	2.66	4.69	4.32	43.2	.58
2-J	81.0	43.1	3.17	2.72	4.48	3.93	39.8	.66
3-J	80.0	44.5	3.24	2.70	4.41	3.78	37.8	.69
4-J	82.2	41.6	3.20	2.85	4.41	3.65	36.5	.82
5-J	81.9	43.4	3.16	2.70	4.17	3.28	32.8	.79
6-J	80.8	41.9	2.90	2.56	3.88	2.86	28.6	.76
7-J	79.4	43.4	2.94	2.51	3.85	2.70	27.0	.76

EXPLANATION OF GRAPH SYMBOLS

In the following graphs the experimental runs are referred to by letter, and the letters designate the following:

A* = Pulp + alum + 2% Kymene (Kymene/pulp) + separate addition of 10% TiO_2 (TiO_2 /pulp).

B* = Pulp + alum + 2% Tydex (Tydex/pulp) + separate addition of 10% TiO_2 (TiO_2 /pulp).

C* = Pulp + alum + (10% TiO_2 and 2% Kymene in a slurry) (Kymene/ TiO_2)

D* = Pulp + alum + (10% TiO_2 and 2% Tydex in a slurry) (Tydex/ TiO_2)

* In runs A, B, C, & D the pH is controlled by alum addition.

E, F, G, & H = Pulp + alum + (10% TiO_2 and 2% Kymene in a slurry) (Kymene/ TiO_2) and pH is controlled by NaOH and H_2SO_4 independently from the percent of Alum present.

E= 0% Alum, F= 2% Alum, G= 4% Alum, and H= 6% Alum

I* = Pulp + alum + (10% TiO_2 and 2% Kymene in a slurry) (Kymene/ TiO_2)

J* = Pulp + alum + (10% TiO_2 and 2% Tydex in a slurry) (Tydex/ TiO_2)

* In runs I & J the alum controls pH until sheet formation where all sheets are adjusted independently of alum to pH 5.5.

Graphical Results of TiO_2 retention versus pH
at time of TiO_2 addition.

pH Controlled with alum

% Alum Added to Pulp

0 1 2 3 4 5 6

Percent TiO_2 Retained

70

60

50

40

30

20

7

7

6

5

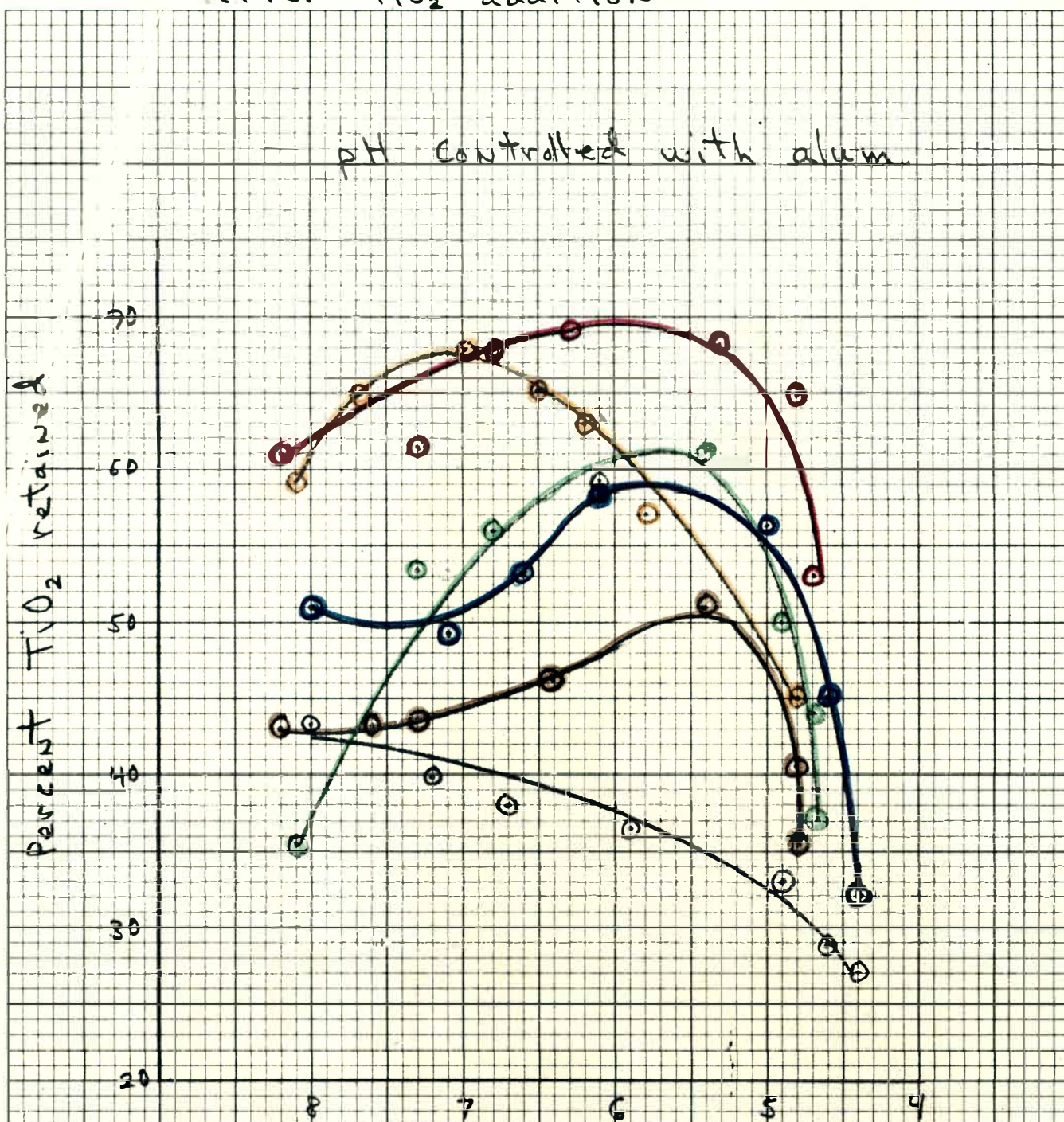
4

pH at TiO_2 addition

- A = (Pulp + Alum + Kymene) + (TiO_2 slurry)
- B = (Pulp + Alum + Tydex) + (TiO_2 slurry)
- C = (Pulp + Alum) + (TiO_2 + Kymene slurry)
- D = (Pulp + Alum) + (TiO_2 + Tydex slurry)
- I = (Pulp + Alum) + (TiO_2 + Kymene slurry)*
- J = (Pulp + Alum) + (TiO_2 + Tydex slurry)*

* pH adjusted to 5.5 before sheet formation.

Graphical Results of TiO_2 Retention versus pH after TiO_2 addition



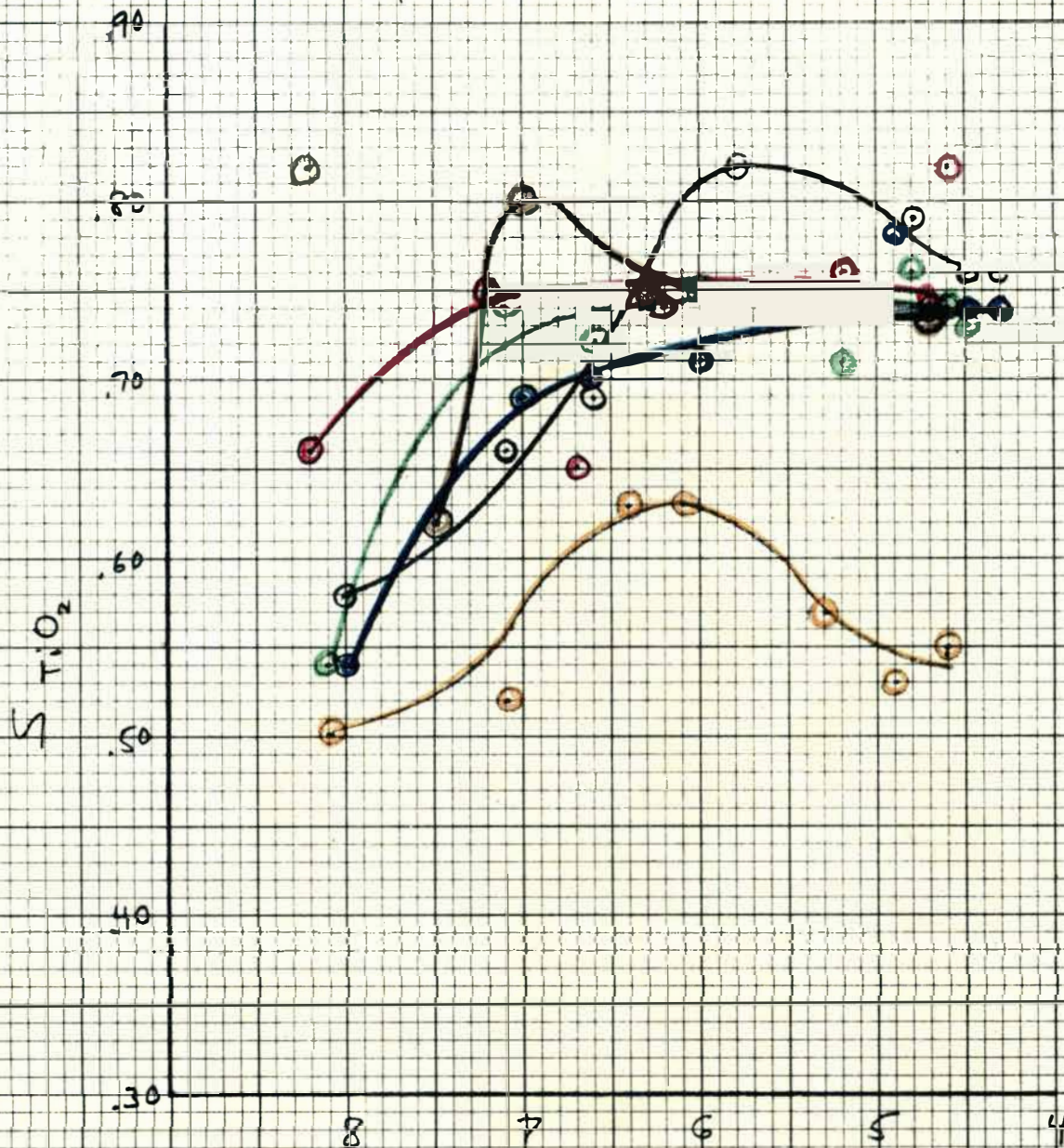
pH after TiO_2 addition

- A: (Pulp + Alum + Kymene) + (TiO_2 slurry)
- B: (Pulp + Alum + Tydex) + (TiO_2 slurry)
- C: (Pulp + Alum) + (TiO_2 + Kymene slurry)
- D: (Pulp + Alum) + (TiO_2 + Tydex slurry)
- E: (Pulp + Alum) + (TiO_2 + Kymene slurry) *
- F: (Pulp + Alum) + (TiO_2 + Tydex slurry) *

* pH adjusted to 5.5 before sheet formation.

Graphical Results of scattering coefficient of TiO_2 versus pH at time of TiO_2 addition

pH Controlled with Alum



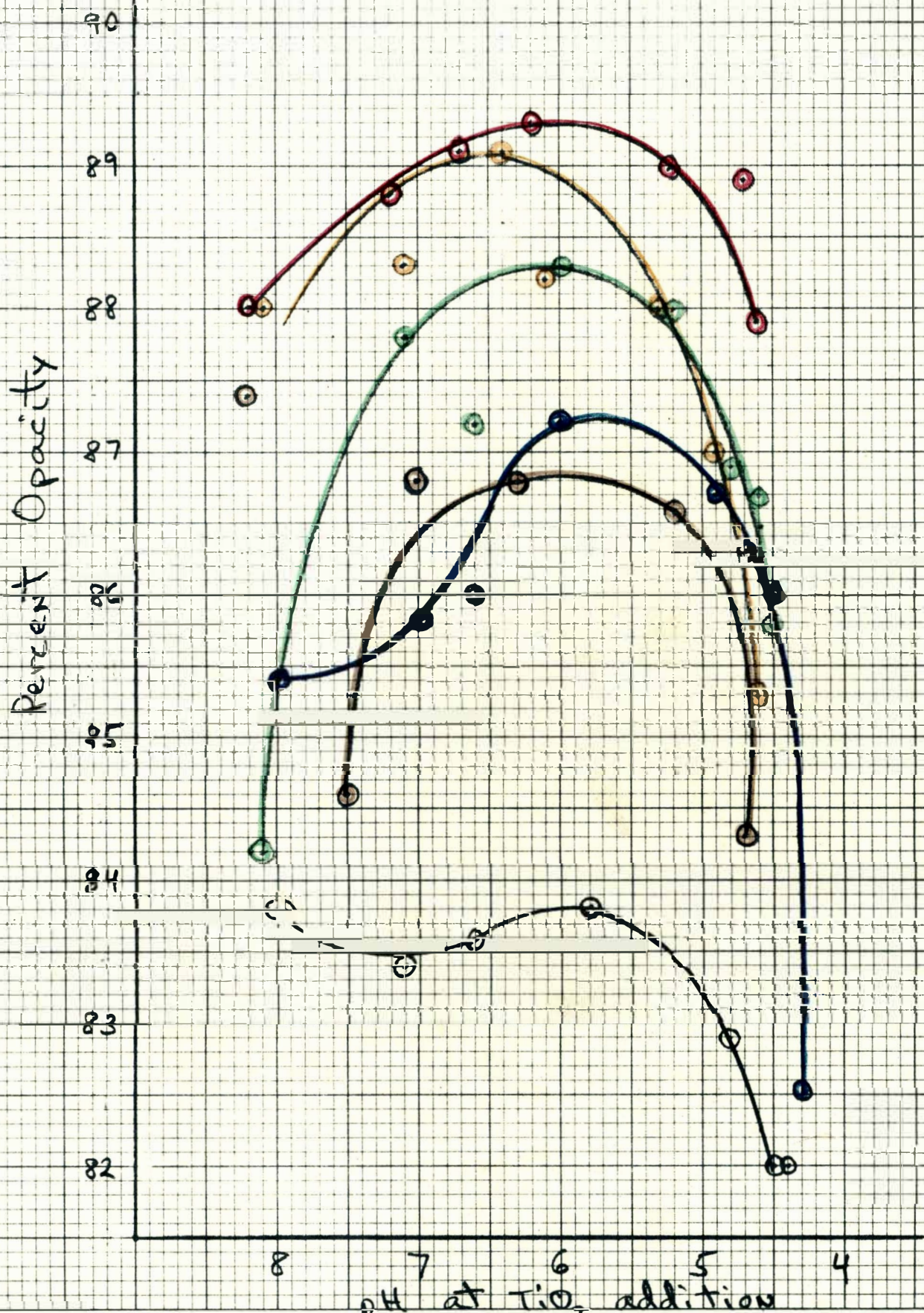
pH at TiO_2 addition

- A = (Pulp + Alum + Kymene) + (TiO_2 slurry)
- B = (Pulp + Alum + Tydex) + (TiO_2 slurry)
- C = (Pulp + Alum) + (TiO_2 + Kymene slurry)
- D = (Pulp + Alum) + (TiO_2 + Tydex slurry)
- I = (Pulp + Alum) + (TiO_2 + Kymene slurry) *
- J = (Pulp + Alum) + (TiO_2 + Tydex slurry) *

* pH adjusted to 5.5 before sheet formation

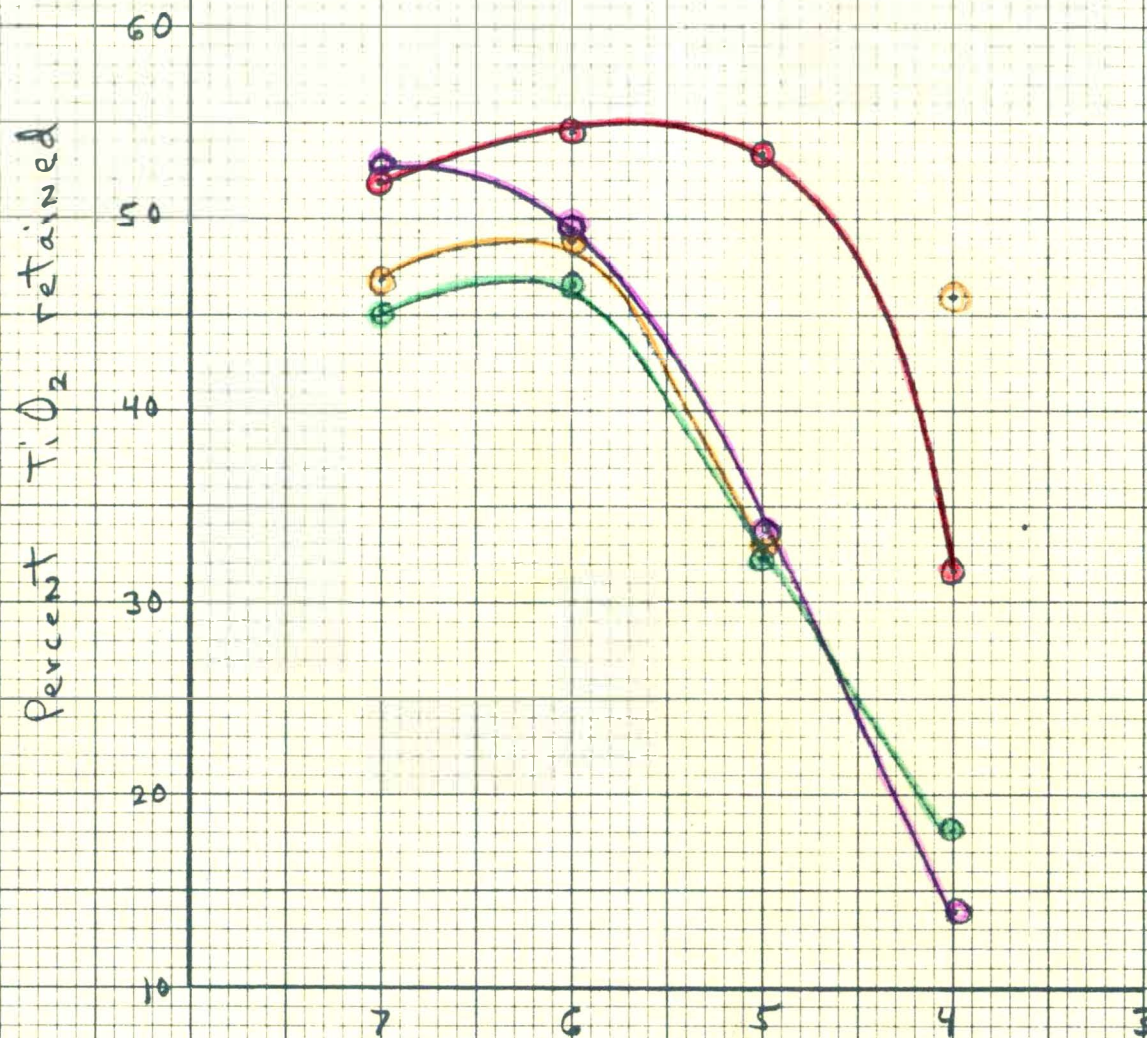
Graphical Results of opacity of sheet versus pH at time of TiO_2 addition

pH Controlled with alum



Graphical Results of TiO_2 Retention versus pH which was constant from TiO_2 addition thru sheet formation.

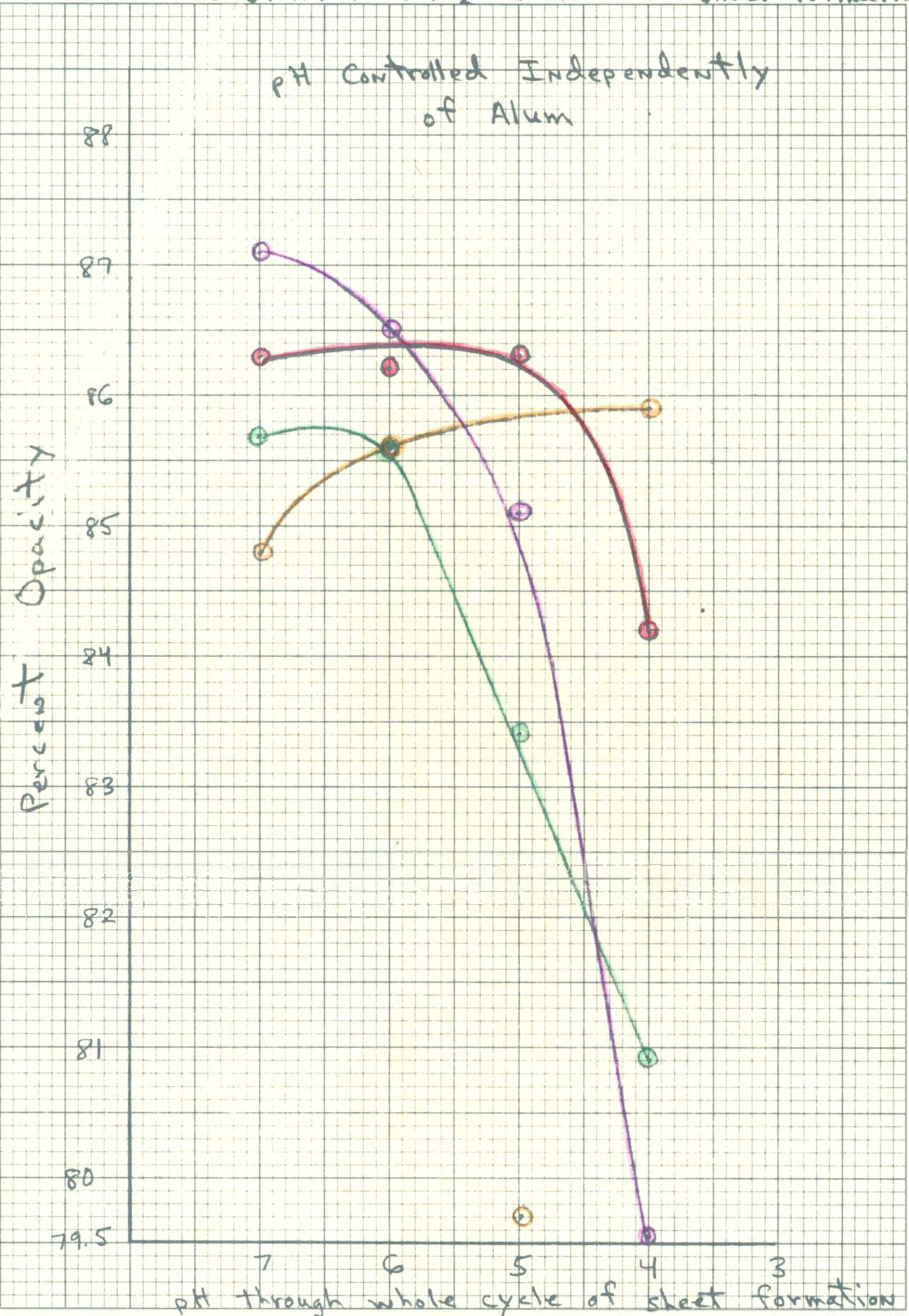
pH Controlled independently of alum



pH through whole cycle of sheet formation

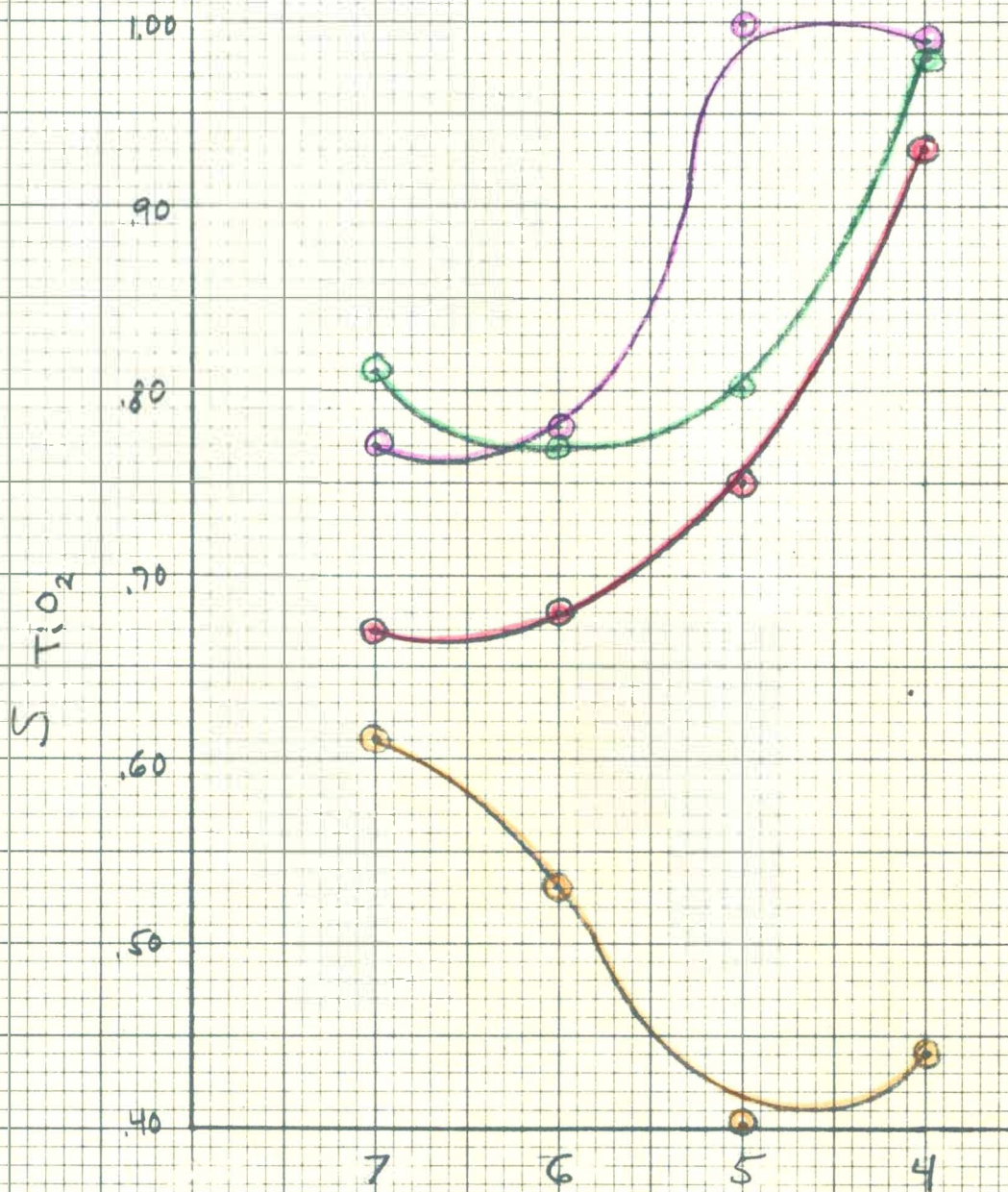
- E = 0% Alum
- F = 2% Alum
- G = 4% Alum
- H = 6% Alum

Graphical Results of Percent Opacity versus pH which was constant from TiO_2 addition thru sheet formation



Graphical Results of scattering coefficient of TiO_2 versus pH which was constant through sheet formation cycle

pH Controlled Independently of Alum

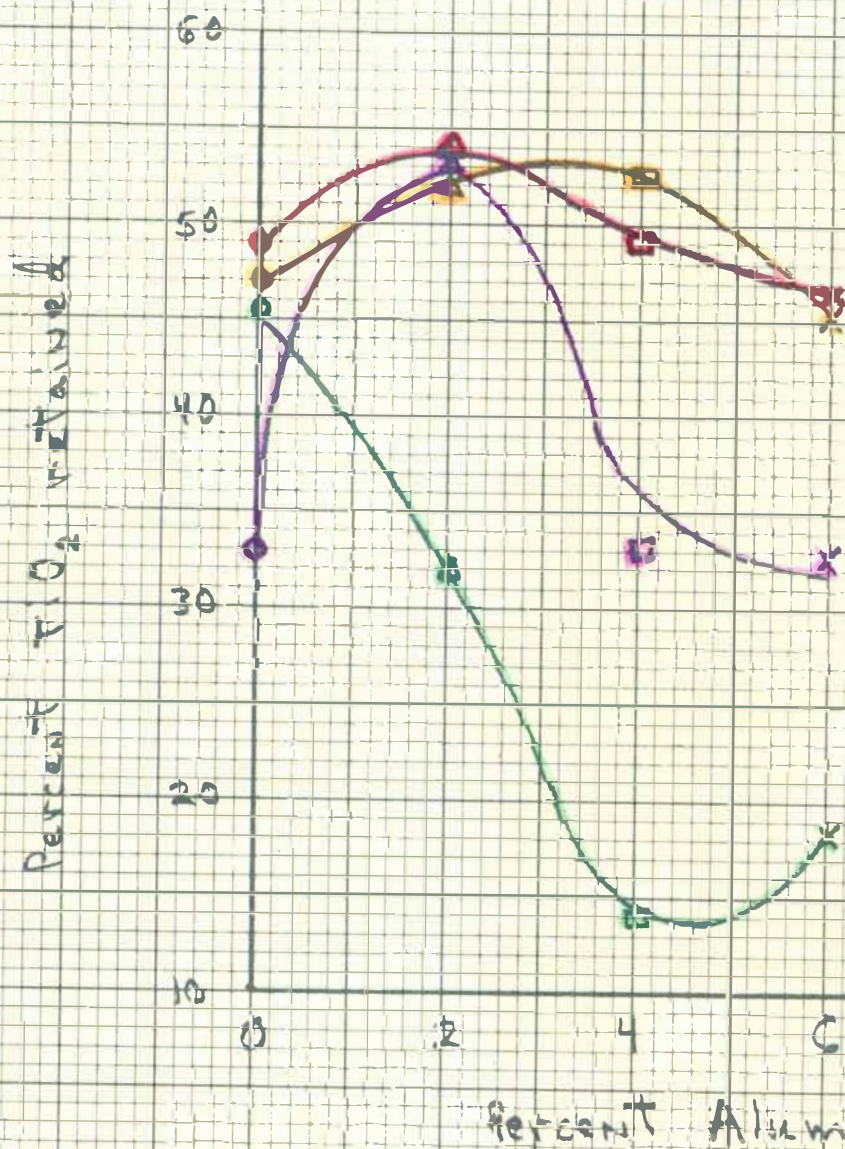


pH through whole cycle of sheet formation

- E = ——— 0% Alum
- F = ——— 2% Alum
- G = ——— 4% Alum
- H = ——— 6% Alum

Graphical Results of TiO_2 retention versus percent Alum added.

pH Controlled independently of Alum



pH 7.0 —
 pH 6.0 —
 pH 5.0 —
 pH 4.0 —

Data from sample
 H = 0
 H = 1
 H = 2
 H = 3

BIBLIOGRAPHY

1. Nelson, J.R., Paper Trade Journal, 142, (34): 41-43 (December 16, 1968).
2. Thode, E.F., Htoo, S., TAPPI, Vol 38, No. 12, 705-709 (1955).
3. Nelson, J.R., Jurisch, M.J., Paper Trade Journal, Vol. 148, No. 38, 39-42 (September 21, 1964).
4. Boots, L., "Development of a New Retention Aid", TAPPI, Vol. 43, No. 10, 859-860, (October 1960).
5. Date, J.S., Snute, J.M., TAPPI, Vol. 42, No. 10, 824-826 (1959).
6. Fraik, R.D., "Some Elements of Filler Retention", TAPPI, Vol. 45, No. 8, 159-164a, (August 1962).
7. Swanson, J.W. and Williams, D.G., "Particle Retention in Paper making Systems", TAPPI, Vol. 45, No. 8, 147-151, (April 1966).
8. Willets, W.R., Paper Trade Journal, Vol. 102, No. 3, 36-39, (January 16, 1936).
9. Haslam, J.H., Steele, F.A., Paper Trade Journal, Vol. 102, No. 25, 22-25, (January 9, 1936).
10. Brill, H.C., "Evaluation of Beater Retention Aids", TAPPI, Vol. 38, No. 9, 522-526, (September 1955).
11. Mysels, K.J., Introduction to Colloid Chemistry, New York, Interscience, pp. 359-384, (1959).