10-1972

The Effect of PH on Retention Aids: A Study of Retention, Optical Efficiency and Filler Distribution

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"THE EFFECT OF pH ON RETENTION AIDS: A STUDY OF RETENTION, OPTICAL EFFICIENCY AND FILLER DISTRIBUTION"

by

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A Thesis Submitted To The Department
of Paper Science and Engineering
in Partial Fulfillment of the
Degree of Bachelor of Science

Western Michigan University
Kalamazoo, Michigan

October, 1972

ABSTRACT

This paper was designed to develop insights on the retaining, optical efficiency and filler distribution properties of retention aids at various pH levels. Three leading retention aids; Cato 15, Natron 86 and Nalco 623 were studied in the normal papermaking pH range 3.5 to 6.5 to determine the effect of pH.

The results indicated pH played an important role in producing conditions of optimum retention and optical efficiency. pH also contributed to the distribution of the filler in the handsheets. The results further indicated, when using retention aids, optimum retention of titanium dioxide does not always yield the highest scattering coefficients. Furthermore, it was found higher scattering coefficients resulted in handsheets without retention aids than in handsheets using retention aids, if the sheets contained the same amount of titanium dioxide.

The pH levels at the time of sheet formation where maximum retention existed for Cato 15, Natron 86 and Nalco 623 were 5.5, 4.5, and 6.0. While the pH levels for optimum scattering coefficients for Cato 15, Natron 86 and Nalco 623 were 6.5, 6.5 and 4.0 respectively.

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INTRODUCTION

The paper industry through the years has experienced many revolutionary changes. One of the most notable changes is the widespread use of finely powdered chemically inert particles which are commonly referred to as fillers. It has been through the use of fillers that the "quality" of the various grades of paper has shown remarkable improvements. These improvements in sheet quality are numerous; they include increased brightness and opacity, improved ink receptivity, improved sheet smoothness, improved formation and better calendering properties.

Fillers, however, have brought problems into the paper industry. Areas such as economics, equipment development and water pollution have all been given a great deal of attention. In view of these aspects it is not surprising that the introduction of fillers paved the way for another revoluntary development. The use of retention aids which is the basis for the topic of this study.

LITERATURE SURVEY

Fillers

There are many types of fillers. Included are clay, titanium dioxide, calcium carbonate, hydrated aluminum oxide, calcium sulphite, talc, asbestos and many others. This wide selection requires the papermaker to define the various properties he wishes to impart to the sheet, through the use of fillers. Fillers vary in refractive index, brightness, particle size and specific gravity. It is up to the papermaker to determine the filler which will allow him to produce the sheet properties which are specified. This is further complicated by the cost factor, which is of prime importance in any mill operation.

It can easily be seen that the various grades of paper will constitute different filler requirements. In light of this Willets (1) speculated on the characteristics of the "perfect filler".

1. It should have a reflectance of 100% in all wavelengths of light so that it would have maximum brightness and whiteness.
2. It should have a very high refractive index so that it would have maximum opacifying and brightening power.
3. It should be completely free from grit or extraneous matter and have a particle size distribution close to 0.3 microns, approximately half the wavelength of light.

4. It should have a low specific gravity and be soft and non-abrasive.
5. It should be capable of imparting to paper a surface capable of taking any finish from the lowest matte to the highest gloss.
6. It should be completely chemically inert and insoluble.
7. It should be completely retained in the paper web so that there would be no loss to the white water system.
8. It should be reasonable in price.

The first six specifications relate directly to the physical properties that the "ideal filler" should impart into the sheet itself. The last two criteria, retention and cost are only indirectly related to sheet quality. However, these two factors are rapidly becoming the most important considerations. The reason for concern over these two factors is due to two areas of development. First, the economics of reclaiming nonretained filler are to be preferred over sending filler losses to the sewer. This is due to filler cost increases and the widespread use of the more expensive loading materials.

The second development is the concern about ecology which has made untenable the paper industry's use of the streams, rivers and lakes which were previously used for disposing of mill wastes. It is these two developments that have prompted this research on retention aids. The role of pH and the determination of filler distribution in the presence of retention aids are the two factors studied in hopes of gaining knowledge in the maximum utilization of fillers.

Filler Retention

There are a number of definitions for filler retention, but basically percent retention can be defined as the ratio of filler in the finished product to the amount of filler added multiplied by 100 per cent. Retention is dependent on factors dealing with collodial chemistry; flocculation, co-flocculation and electrostatic adhesion (2). The simple mechanical filtration where particles are trapped in the web as well as the hydraulis of the paper machine and related equipment also play a major role in retention. Willets (2) states that probably the latter involving white water recovery efficiency plays the largest role.

Mechanisms of Retention

The retention of fillers appears to be due to a combined mechanism. Physicochemical as well as mechanical factors play an important role in the retention of filler in the paper web.

Electrostatic Attraction

When two phases of different chemical constitution come in contact, such as fiber and water or filler and water, the development of an electrical potential difference exists between the two phases. This potential difference is called the zeta potential. It was indicated by Thode and Htoo that when pulp is dispersed in water a negative potential difference develops leaving the fibers with a negative charge (3).

Titanium dioxide, clay and other fillers commonly used in papermaking also develop a negative zeta potential when dispersed in water. The charge of the zeta potential is an indication of the surface dominating ions. Negative zeta potentials indicate anions dominate the outside of the potential gradient. Whereas, positive zeta potentials indicate cations dominate the outside (4). When the zeta potential is zero, this indicates the isoelectric point. It is at the isoelectric point where maximum flocculation will occur (5).

One of the important factors which effect the zeta potential is pH (2). It must be noted that cellulose in water over most of the pH range retains a negative charge (5). This coupled with the fact that titanium dioxide in the papermaking pH range also develops a negative charge, illustrates why retention is difficult to achieve in a fiber-filler suspension.

Retention aids are one way of improving the adverse electrostatic conditions which exist in the papermaking system. The addition of the various retention aids, which are also known as flocculating agents, bring the zeta potential close to zero and induce flocculation of both fillers and fibers. High molecular size materials such as cationic agent are believed to bridge negatively charged fiber and filler together in the furnish. Here, the size of the molecule and its charge effect are both important factors in bridging. Alum, on the other hand does not have a high molecular weight, however, under proper pH conditions alum will flocculate filler and fiber into large colloidal particles. This enables alum to bridge negatively charged particles in the furnish. In the case of fiber to filler bridging a co-flocculation or electrostatic cementing takes place. This is the same type of electrostatic cementing that takes place in flocculation.

Oakleaf (6) indicated through the use of cationic agents, the zeta potential of the titanium dioxide particles can be changed to positive values. This seemed to indicate the higher the positive zeta potential the retention aid imparted to the filler, the more efficient it becomes in the mechanisms of flocculation and co-flocculation.

It has been established that electrostatic forces play an important role in retention. This mechanism was based on the premise that maximum flocculation, was accomplished by approaching the iso-elective point of the suspended filler (5). Co-flocculation was accomplished by changing the zeta potential of either fiber or filler to a positive value. Thus, a negative-positive-negative situation was produced allowing for the fiber-retention aid-filler floc to be produced. If only electrostatic considerations are responsible for retention, there would be essentially no retention in the presence of adverse electrostatic conditions. However, this is not the case and the other aspects of retention should be viewed at this point.

Mechanical Filtration

When only fiber and filler are present in the system the retention will be an almost complete mechanical phenomenon (2). Retention through filtration requires that the filler particles be larger than the interstices between the fibers. The methods of improving retention through the mechanism of filtration are varied, but all have to do with either decreasing the openings between fibers or increasing the pigment particle size. Hydration and fibrillation resulting from refining (2), the addition of fines (7), and increasing basis weight (8) will act to increase retention through mechanical filtration. Whereas high machine speeds, rapid drainage, high degree of suction and severe agitation will tend to lower retention (2). Insofaras the pigment itself is concerned, large particle size and low specific gravity will be assets in retaining filler (2). The flocculation of fillers producing larger pigment agglomerates will obviously be of great benefit to mechanical filtration (2) and illustrates the interdependence of the physiochemical and mechanical factors which combine in the mechanism of retention.

Retention Aids

The use of retention aids in the industry has become widespread. Chemical addition for the purpose of better retention involves various groups of compounds which enhance the conditions for retention. This is primarily in the area of electrostatic attraction and bridging so maximum flocculation and co-flocculation can exist.

There are many retention aids on the market. Nelson (7) breaks these compounds into four basic groupings.

1. Inorganic salts - alum and sodium aluminates. There are recognized limitations to their contributions due to effects on total acidity and corrosion. Their low molecular weight provide only limited bridging effects only if proper pH conditions are present.
2. Naturally occuring organics. Starches and gums have done the job. However, they do reduce drainage on the wire.
3. Chemically modified organics. Cationic, anionic and non-ionic modified starches and gums. However, starches and gums contribute to B.O.D. problems.
4. Synthetic organics - these include cationic, non-ionic and anionic high polymers. In this area are the greatest opportunities for results. They are specifically designed and present greatly reduced B.O.D. problems.

The retention aids used in this study are: Cato 15, a cationic starch, Nalco 623, an anionic polymer and Natron 86 a cationic polymer. Cato 15 and Natron 86 were manufactured by National Starch and Chemical. While Nalco 623 was manufactured by the Nalco Chemical Company.

Cato 15, which is a cationic starch is applied in the areas of fiber bonding and fine and filler retention. Nalco 623 is furnished in liquid form. The high molecular weight anionic polymer is sensitive to pH. It is applied for increased drainage, improved formation, and its retention of fines and fillers. It is also used in save-all operations. Natron 86 is a polyelectrolyte flocculant of moderate molecular weight. It has found application in the areas of retention, drainage, strength and save-all operation.

Factors Affecting Retention

There has been a number of studies on the factors which are believed to cause retention differences. Willets (8, 9) published papers in the mid 1930's which focused primarily on the retention of titanium dioxide and revealed the following conclusions:

1. Retention was increased by the use of alum up to about three percent based on the weight of the fiber. Beyond this point the retention decreased slightly. Rosin, when used with alum, increased the retention, however alum, appeared to be the most important factor (2).
2. The use of starch will produce a deleterious, rather than a beneficial effect of retention.
3. Surface area development due to beating caused marked retention improvements.

4. Increased basis weight produced retention increases, especially at lower weight.
5. Temperature increases caused marked increased in retention.
6. Dilution at the sheet machine caused increased retention, this was probably related to pH changes.

In 1955 Brill (7) did further work in the area of starch effects on titanium dioxide retention. He found; (1) retention was seriously reduced by many forms of beater added corn starch if added in the cooked form. This confirmed previous investigations. (2) hypochlorite oxidized corn starch reduced the retention of pigments and ranked as one of the worst offenders. (3) cationic starch and sodium pospho-aluminate produced the best retention in the presence of oxidized corn starch.

Fraik (5) studied titanium dioxide and concluded:

1. Retention appeared to be a function of the pH encountered when the pigment was added to the system.
2. Maximum retention for the titanium dioxide studied occurred when this pH was in the range of five to six.
3. Alum content did not correlate with retention in systems where pH was dependent on alum.
4. The order in which alum and titanium dioxide were added to the system affected the retention and optical efficiency of the pigment.

5. Pigment retention was affected by subsequent pH changes after the alum was added to the system.
6. Chemicals such as sodium hydroxide, sulfuric acid and rosin size affected retention.
7. Retention was improved by the adjustment of pH with electrolytes other than alum.

Brill and Hecklau (14) later found (1) severe agitation markedly lowered the retention of titanium dioxide when starch was present, (2) an increase in clay content did not appreciably change the retention of titanium dioxide, and that starch has a greater effect on titanium dioxide retention than on clay retention, (3) the dilution of the furnish following flocculation appreciably affected retention in the absence of starch and only reduced retention slightly when starch was present and (4) increased temperature reduced retention only slightly in the presence of starch but had no effect when starch was not present.

Machine operations as they affect retention presents another group of very important parameters. Increases in speed, degree of suction, and turbulence will decrease retention (2). Filler characteristics also contribute to the degree of retention. Fillers which have large particle size, low specific gravity or a combination of both will be better retained (2). The shape of the filler may also play an important role as evidenced by the retention qualities of the skeletal.shaped fillers such as diatomaceous earth and asbestos which are being used (12).

The primary factors which affect retention can be summarized in the following fashion. The order, however, may not be indicative of the individual importance as this is based on the particular situation.

1. Mechanical operating parameters.
2. Beating and the presence of fines.
3. Concentration of reactants and alum in the furnish.
4. Sequence of chemical addition.
5. Temperature, agitation, and dilution.
6. Physical characteristics of the filler.
7. Presence of starch and other additives.
8. Use of retention aids.

One important factor which effects retention that was not included in this list is pH. The pH variable was the basis for this study and will be reviewed separately in the following section.

Effects of pH

There has been a great deal of study on the effects of pH in alum systems on retention. However, the pH values where maximum retention and opacity exist using some of the newer retention aids have not been as closely defined. There has been work showing the effect of pH and alum loading on polyacrylamide (13). This work indicated maximum retention at pH 6 with 2-3% alum and that greater retention took place at higher pH with higher alum loadings. There is data, however, which shows a point where increased alum addition, regardless of pH, will result in decreasing retention (5). Swanson and William (14) found that any pH adjustments should be accomplished before the polymer solution is added when the filler is contained in the furnish.

In alum systems without the presence of other retention agents a great deal has been found about the effects of pH and alum concentration. Willets (1) found that 2.5 to 3 per cent alum based on the fiber in a pH range of 5.0 to 5.5 gave maximum retention for titanium dioxide. These conditions for maximum retention varied with operating conditions. This may account for the fact that Brill and Hecklau (11) reported 1 to 2 per cent alum produced maximum titanium dioxide retention.

Fraik (5) did a study on pH conditions which were independent of alum. He concluded that pH controlled after alum and filler had been introduced affected retention. This effect shifted the retention curves up or down. He reported that pH of 5.0 to 6.0 produced maximum retention. He also did a study which showed the relationship between retention and amount of alum did not exist. He also found a relationship existed between retention and pH at the time of filler addition.

In the area of cationic retention aids, Oakleaf (6) did a study with Hercules Inc's. Kymene 557 (Epichlorohydrin) and Dow's Tydex (Polyethylenimine). He found that pH controlled by alum produced higher titanium dioxide retention and opacities as opposed to when pH was controlled independently of alum. He found that pH of 5.7 produced the maximum titanium dioxide retention before the titanium dioxide - cationic agent was added. However, by retaining this pH at the time of sheet formation, the cationic agent suffered in efficiency. He also found that pH of 6.0 produced the maximum opacity. In the light of the fact the optimum retention of filler was produced at pH of 5.7, it brings to question how the retention aid distributes the filler in the sheet. This was the other aspect of the study. Noting that pH was an operating variable that should be studied for each retention aid that was entered into the system.

PRESENTATION OF PROBLEM

In view of the fact previous investigators had indicated pH was an important consideration in their studies of titanium dioxide retention, this paper was designed to determine the pH levels where Cato 15, Natron 86 and Nalco 623 yielded the highest retentions and the maximum optical efficiency. This study was also designed to evaluate the effects on filler distribution in the sheet which might result from the use of the individual retention aids. The study of filler distribution would also be an indication of the degree of improvement in optical efficiency caused by evening the pigment profile throughout the sheet.

EXPERIMENT DESIGN

Evaluation of the Effect of pH on Retention Aids

In order to study the effect of pH, the three retention aids were applied over the normal papermaking pH range of 3.5 to 6.5. The pulp used was fifty percent Allied Paper Company southern bleached hardwood kraft and fifty percent Celgar Canadian bleached softwood kraft. The pulp was refined according to Tappi Standard T 200 OS 70 to a C.S.F. of 375. Deionized water was used throughout the experiment to eliminate the water hardness variable. Two percent alum and one percent rosin based on the oven dry weight of the pulp were used as standard additives. Sulfuric acid and sodium hydroxide were used to control the pH after the point of alum addition.

Ten percent anatase titanium dioxide based on the oven dry weight of the pulp was chosen as the amount of pigment added to the pulp slurry. This figure was chosen because it was felt variations in the amount of filler retained at this level could easily be recognized. The titanium dioxide suspensions were made in large batches and kept under constant mixing.

The retention aids were added to the accurately measured titanium dioxide suspensions in dropwise fashion under a constant degree of blending. The retention aids were added in this fashion because previous thesis work had indicated this method to be more efficient with respect to titanium dioxide retention (6). Two-tenths percent retention aid based on the oven dry weight of fiber was used for each pH level. This value was typical of the concentration used in industry. It was kept constant so comparisons could easily be made.

The titanium dioxide suspensions were blended for an additional sixty seconds after the addition of the retention aids. After this light mixing the titanium dioxide was added to the pulp slurry which had previously been adjusted for pH. The slurry with the titanium dioxide was allowed to mix for an additional two minutes. After this additional mixing the slurry was taken to the sheet machine where the dilution water had been adjusted to the corresponding pH. Standard Noble and Wood handsheets was then made from the pulp slurry. In one group of samples for Cato 15 the dilution water was not pH adjusted so a comparison could be made between pH at the time of retention addition versus pH at the time of sheet formation.

The handsheets were conditioned and weighed (Tappi T-404 m-49) and tested for brightness (Tappi T-402 m-49), opacity (Tappi T-425 m-60) and per cent ash (Tappi T-413). From this data the percent retention of titanium dioxide and basis weight of the sheet were calculated and the optical comparisons were made.

Determination of Filler Distribution

In the determination of filler distribution, the effects of the retention aids were evaluated by making handsheets in the same fashion as the pH study. Two pH levels were studied in the evaluation of the retention aids effects on filler distribution. The two pH levels corresponded to the pH of maximum retention and the pH of maximum opacity for each retention aid. These pH values were chosen because it was felt they would exemplify changes in filler distribution if the changes existed.

The only difference in the handsheet procedure for the filler distribution study was with respect to the amount of titanium dioxide added to the pulp slurry. The correct amount of titanium dioxide was added to the pulp so approximately eight percent of the oven dry weight of the sheet was pigment. The value for the pigment addition was estimated from the percent retention values of the pH study. Adjustment were made based on the resulting percent filler results.

The handsheets were conditioned and tested according to the same procedures as the pH study. They were then split into four sections using the Beloit Sheet Splitter. The split sections were then ashed to determine titanium dioxide in each section. The sheet splitter was also used to prepare half sections of the handsheets for opacity and brightness measurements.

PRESENTATION AND DISCUSSION OF RESULTS

Retention as a Function of pH

When comparing the percent retention utilizing a retention aid to the percent retention of a standard using no retention aid a marked difference was illustrated when the standard data in Table I was compared to the retention aid data in Tables II, III, IV, and V. This was expected so other properties of retention aids were also evaluated in this study. The important aspects which were evaluated in this study are the overall performances of the individual retention aids at the various pH levels. This was based on the percent retention, the effect on optical properties and the effect on two-sidedness.

The data in Tables II, III and IV clearly indicate each retention aid has a pH level where it's function as a retaining agent is optimum. This is also illustrated in Figure 1. Cato 15 appears to give its optimum retention at pH 5.5, while Natron 86 and Nalco 623 yielded their highest retentions at pH 4.5 and 6.0 respectively.

These values are not exact optimums but the data in Figure 1 clearly indicates these values are indicative of the optimum points.

Analyzing the pH vs retention curves of Figure 1, the retention appears to follow a linear pattern with respect to pH in certain ranges for each retention aid. After the optimum retention is reached in the case of Cato 15 and Nalco 623, sharp decreases in retention occurred in what appeared to be a linear function. Nalco 623 also appeared to be

Table I

Analysis of Standard Handsheets Containing No Retention Aids Using The Same Amount of Pigment As In The pH Study

STANDARD VALUES

Per cent retention	26.29
Wire side brightness	83.81
Felt side brightness	83.30
Opacity	83.08
Sheet weight	2.5109
S_x felt side	2.77
S_x wire side	2.74
S felt side	0.224
S wire side	0.221

Table II

Analysis of Cato 15 over pH Range
3.5 to 6.5 at the Formation of the Handsheet

pH	Brightness Felt	Brightness Wire	Opacity	Percent TiO_2 in sheet	Percent TiO_2 Retention	S_x Felt	S_x Wire	S Felt	S Wire
3.5	81.16	81.54	80.56	3.428	34.28	2.42	2.44	0.196	0.198
4.0	80.08	80.60	82.76	3.536	35.36	2.60	2.62	0.210	0.211
4.5	81.28	81.57	82.90	3.526	35.26	2.70	2.72	0.220	0.221
5.0	81.68	82.09	83.30	3.677	36.77	2.75	2.78	0.225	0.227
5.5	80.33	80.87	84.08	4.152	41.52	2.84	2.87	0.229	0.232
6.0	80.92	81.32	84.86	3.701	37.01	2.90	2.94	0.234	0.237
6.5	81.90	82.29	85.59	3.428	34.28	3.04	3.08	0.247	0.251

Table III

Analysis of Natron 86 Over pH Range
3.5 to 6.5 at the Formation of the Handsheet

pH	Brightness Felt	Brightness Wire	Opacity	Percent TiO_2 in sheet	Percent TiO_2 Retention	S_x Felt	S_x Wire	S Felt	S Wire
3.5	83.73	84.21	84.88	4.242	42.42	3.08	3.13	0.250	0.254
4.0	83.74	84.10	84.75	4.509	42.09	2.85	2.87	0.230	0.232
4.5	82.60	82.97	85.73	4.829	48.29	3.14	3.18	0.253	0.256
5.0	80.80	81.36	86.94	4.682	46.82	3.23	3.28	0.263	0.267
5.5	80.17	80.92	85.32	4.425	44.25	2.96	3.02	0.239	0.244
6.0	81.10	81.65	83.90	4.011	40.11	2.80	2.85	0.225	0.229
6.5	82.00	82.49	87.44	4.405	44.05	3.33	3.39	0.268	0.273

Table IV

Analysis of Nalco 623 Over pH Range
3.5 to 6.5 at the Formation of the Handsheet

pH	Brightness Felt	Brightness Wire	Opacity	Percent TiO_2 in sheet	Percent TiO_2 Retention	S_x Felt	S_x Wire	S Felt	S Wire
3.5	81.21	81.41	81.32	3.717	37.17	2.45	2.48	0.196	0.19
4.0	80.40	80.58	83.75	4.620	46.20	2.73	2.74	0.220	0.22
4.5	80.50	80.73	82.34	5.280	52.80	2.54	2.55	0.204	0.20
5.0	79.32	79.85	83.68	5.040	50.40	2.65	2.69	0.214	0.21
5.5	79.66	79.99	83.58	5.501	55.01	2.66	2.68	0.215	0.21
6.0	80.05	80.76	83.92	5.778	57.78	2.70	2.74	0.218	0.22
6.5	79.88	80.33	80.20	5.456	54.56	2.29	2.32	0.184	0.18

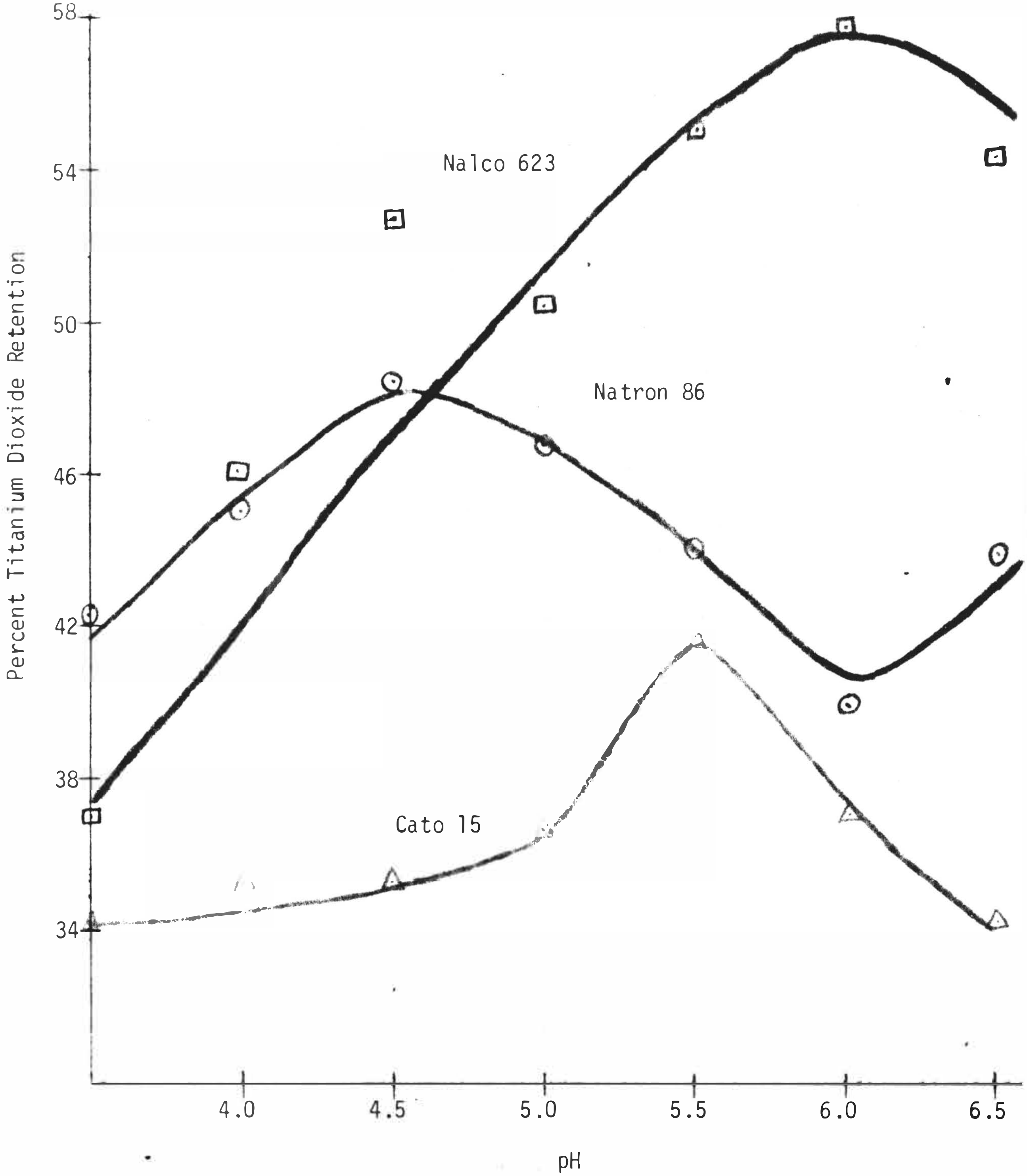
Table V

Analysis of Cato 15 Over pH Range
3.5 to 6.5 At Time of Addition

pH	Brightness Felt	Brightness Wire	Opacity	Percent TiO_2 in sheet	Percent TiO_2 Retention	S_x Felt	S_x Wire	S Felt	S Wire
3.5	80.38	81.57	80.09	3.776	37.76	2.37	2.40	0.193	0.196
4.0	80.78	81.38	80.13	4.098	40.98	2.36	2.39	0.193	0.195
4.5	81.63	82.40	81.36	3.829	38.29	2.54	2.57	0.207	0.209
5.0	82.00	82.63	82.53	3.818	38.18	2.84	2.88	0.227	0.230
5.5	80.10	80.60	83.61	3.544	35.44	2.73	2.75	0.218	0.220
6.0	80.77	81.25	82.20	3.410	34.10	2.54	2.56	0.204	0.205
6.5	82.40	82.89	81.20	3.658	36.58	2.55	2.57	0.206	0.207

Figure 1

The Effect of pH on the Retention of Titanium Dioxide for Cato 15, Natron 86 and Nalco 623



similar in nature. However, the pH range studied in Nalco 623's case should have been extended to pH 8.0, as the peak in this case is at pH 6.0.

It should also be observed that there was a rise in retention at pH 6.5 using Natron 86 after hitting a low point at pH 6.0. This is a rather abrupt reversal and was not noted with the other retention aids. This is another instance where an extension of this project would be of value in yielding further data as the other retention aids were not studied at pH values as distanct from the optimum value. The pH range studied in this project was restricted to the normal pH range of 3.5 to 6.5.

Cato 15 was studied to determine the effect of pH at the time of retention aid addition (Table V). This was to provide a comparison to the data obtained in Table II which indicated the effect of pH at the time of sheet formation. The data shown in Table V was further evidence the pH at the time of formation is the major factor in the retention efficiency of the retention aids. This data indicated pH 4.0 give maximum retention when pH was controlled at the time of retention aid addition. However, when the pH 4.0 slurry was diluted in the sheet mold the subsequent pH was 5.5. This was the pH determined to yield maximum retention when pH was controlled through the time of sheet formation.

Effect of pH on Optical Properties

The effects of the retention aids on brightness, opacity and subsequently scattering coefficient were also listed for Cato 15, Natron 86 and Nalco 623 in Tables II, III and IV respectively. It was most noticeable that the optimum levels of titanium dioxide retention were not always indicative of the highest optical values. In fact only Nalco 623 yielded the highest opacity and corresponding scattering coefficient at the pH level where it's pigment retention was optimum. However, it was shown for the Nalco 623 optical values at pH 6.0 corresponded very closely to the Nalco 623 optical values at pH 4.0, 5.0 and 5.5 where optimum retention was not observed. The scattering coefficient at the corresponding pH levels is graphically presented in Figure 2 for the three retention aids.

An interesting piece of optical information is indicated by the data in Table VI. This data plotted in Figure 3 clearly indicated that it is better from an optical standpoint to use more pigment to retain a fixed amount of titanium dioxide in the sheet than it was to retain the same amount of pigment with the use of a retention aid. Only Cato 15, which in fact yielded the lowest percent retentions, can compare to the optical properties of a standard sheet using no retention aids at an approximately equal titanium dioxide content.

Filler Distribution

The degree of filler distribution in the sheets may be a key to determining why a difference exists between the optical efficiencies of the retention aids. To determine the filler distribution of the samples, the sheets were split into four sections by means of a Beloit Sheet Splitter.

Figure 2

The Effect of pH on the Average Scattering Coefficient for Cato 15, Natron 86 and Nalco 623

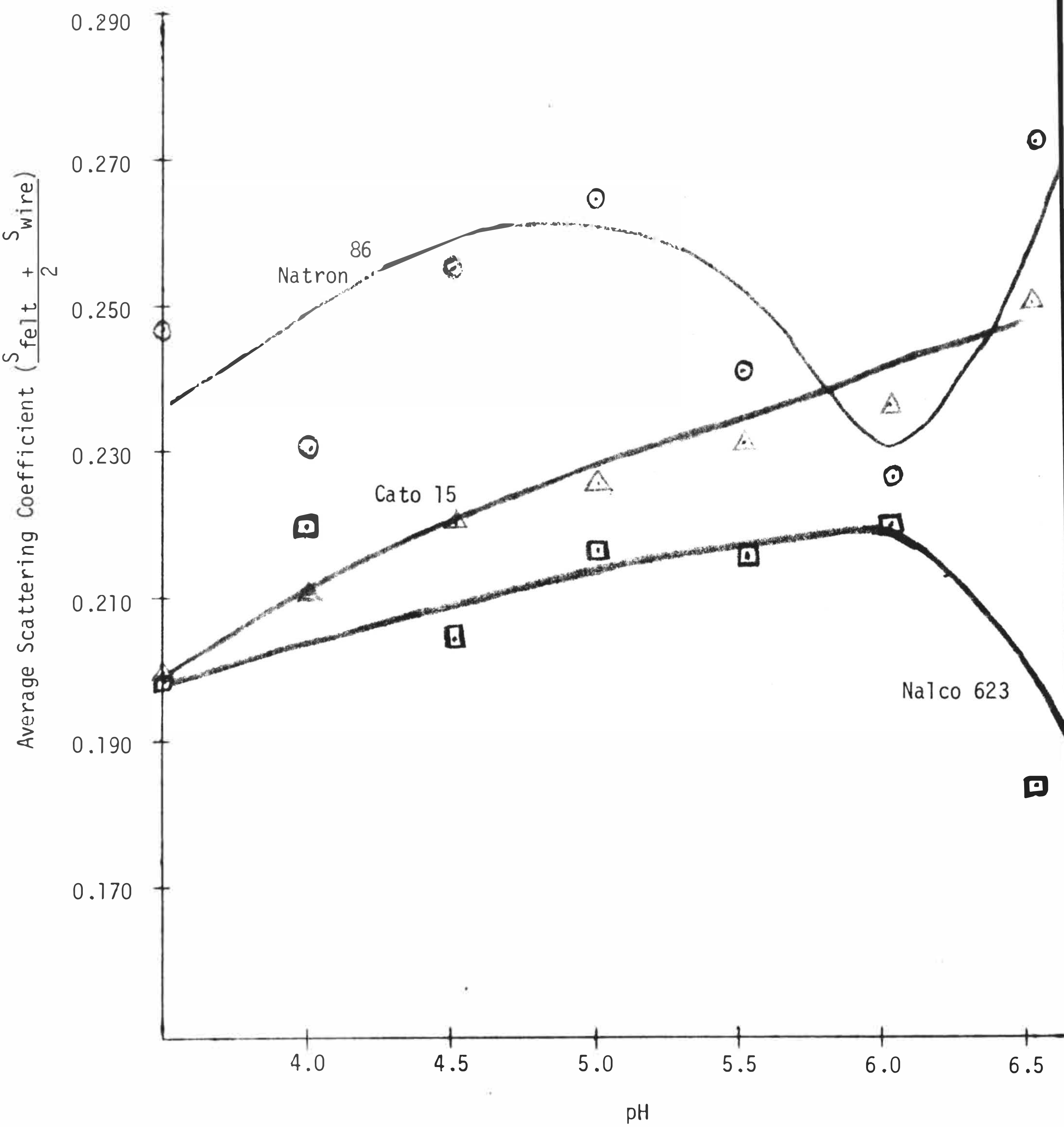


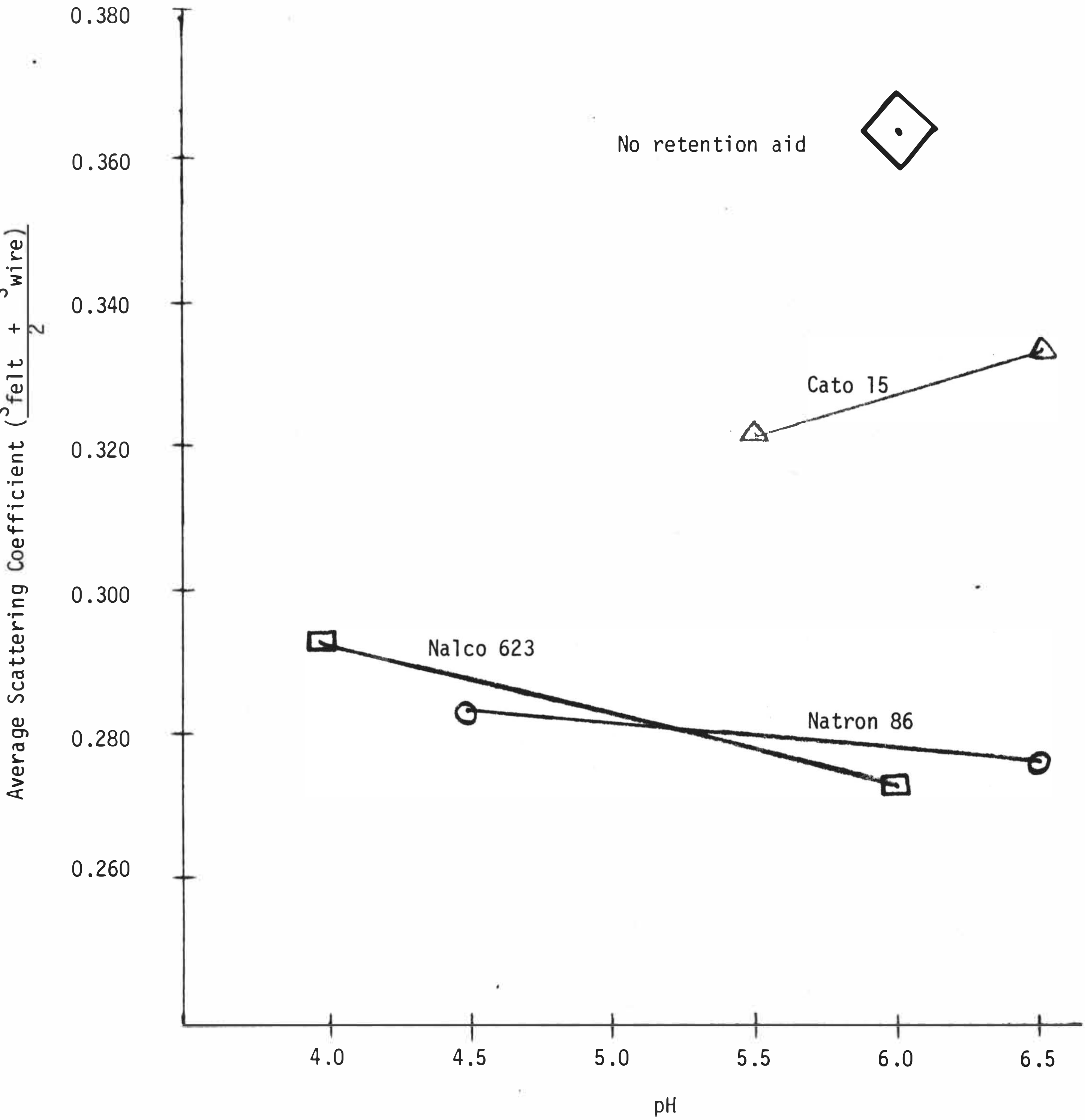
Table VI

Analysis of Retention Aids at Their Optimum pH Levels

Sample	pH	Percent TiO_2 in sheet	Brightness		Opacity	S_x		S	
			Felt	Wire		Felt	Wire	Felt	Wir
Cato 15	6.5	10	92.88	93.77	87.89	4.05	4.10	0.330	0.3
Cato 15	5.5	10	93.89	94.50	87.36	4.00	4.02	0.321	0.3
Natron 86	6.5	10	90.18	90.58	85.29	3.42	3.46	0.274	0.27
Natron 86	4.5	10	91.51	91.85	85.83	3.54	3.56	0.283	0.28
Nalco 623	6.0	10	90.29	90.58	84.70	3.41	3.42	0.273	0.27
Nalco 623	4.0	10	93.39	94.08	85.64	3.60	3.62	0.292	0.29
Standard	6.0	10	88.68	88.38	90.45	4.08	4.10	0.361	0.36

Figure 3

The Effect of Retention Aids
on Average Scattering Coefficients
of Ten Percent Titanium Dioxide
at Various pH Levels



The sections were not exactly quarter sections, however, the individual levels for the different sets of data were close enough with respect to weight so that comparisons could be made and trends spotted. The first level (top level) and the fourth level (wire level) yielded the most information in determining filler distribution. The data is listed for Cato 15 pH 5.5 and 6.5 in Tables VII and VIII respectively. The data for Natron 86 pH 4.5 and 6.5 was listed in Tables IX and X respectively. The data for Nalco 623 pH 4.0 and 6.0 was listed in Tables XI and XII respectively and the data for the standard samples using no retention aids is listed in Table XIII.

The data in Tables XI and XII indicated Nalco 623 decreased two-sidedness in the web of laboratory handsheets. The top layer of the Nalco 623 samples which corresponds to the felt side of a papermachine despite being lower in weight, clearly contained more filler than corresponding top layers of the standard samples. Consequently the bottom level, which corresponds to the wire side of a papermachine, despite being generally higher in weight contained less titanium dioxide. This is exemplified by comparing samples 1 and 3 from Table XIII to samples 3 and 4 from Table XI and samples 2 and 4 from Table XII. These samples also indicated there is greater amounts of filler in the second and third layers which are the layers adjacent to the top and bottom layers respectively.

Cato 15 unlike Nalco 623 illustrates a marked difference in filler

Table VII

The Distribution of Ash Using
Cato 15 at pH 5.5

Sample Description	#1		#2		#3		#4	
	Ash	Web	Ash	Web	Ash	Web	Ash	Web
1st Layer	0.0047	0.0791	0.0037	0.0659	0.0035	0.0673	0.0031	0.0507
2nd Layer	0.0054	0.0569	0.0052	0.0547	0.0054	0.0557	0.0043	0.0574
3rd Layer	0.0080	0.0833	0.0081	0.0848	0.0071	0.0840	0.0076	0.0867
4th Layer	0.0083	0.1012	0.0093	0.1127	0.0094	0.1108	0.0087	0.1089
Total	0.0264	0.3205	0.0263	0.3181	0.0254	0.3178	0.0237	0.3127

Table VIII

The Distribution of Ash Using
Cato 15 at pH 6.5

Sample Description	#1		#2		#3		#4	
	Ash	Web	Ash	Web	Ash	Web	Ash	Web
1st Layer	0.0024	0.0604	0.0031	0.0510	0.0030	0.0600	0.0032	0.0674
2nd Layer	0.0038	0.0550	0.0050	0.0658	0.0046	0.0521	0.0047	0.0541
3rd Layer	0.0077	0.0824	0.0079	0.0850	0.0081	0.0839	0.0032	0.0853
4th Layer	0.0121	0.1070	0.0116	0.1050	0.0110	0.1157	0.0114	0.1098
Total	0.0260	0.3048	0.0270	0.3068	0.0267	0.3117	0.0276	0.3166

Table IX

The Distribution of Ash Using
Natron 86 at pH 4.5

Sample Description	#1		#2		#3		#4	
	Ash	Web	Ash	Web	Ash	Web	Ash	Web
1st Layer	0.0025	0.0622	0.0029	0.0552	0.0029	0.0610	0.0030	0.0646
2nd Layer	0.0051	0.0692	0.0041	0.0772	0.0041	0.0527	0.0046	0.0618
3rd Layer	0.0091	0.0855	0.0086	0.0834	0.0092	0.0831	0.0079	0.0900
4th Layer	0.0097	0.1002	0.0105	0.1083	0.0112	0.1033	0.0107	0.1025
Total	0.0264	0.3171	0.0261	0.3239	0.0274	0.3108	0.0262	0.3189

Table X

The Distribution of Ash Using
Natron 86 at pH 6.5

Sample Description	#1		#2		#3		#4	
	Ash	Web	Ash	Web	Ash	Web	Ash	Web
1st Layer	0.0036	0.0638	0.0036	0.0623	0.0053	0.0640	0.0042	0.0671
2nd Layer	0.0050	0.0620	0.0043	0.0506	0.0046	0.0538	0.0048	0.0527
3rd Layer	0.0079	0.0882	0.0085	0.0900	0.0063	0.0890	0.0072	0.0869
4th Layer	0.0094	0.1037	0.0098	0.1163	0.0104	0.1085	0.0106	0.1062
Total	0.0259	0.3177	0.0262	0.3192	0.0266	0.3153	0.0268	0.3139

Table XI

The Distribution of Ash Using
Nalco 623 at pH 4.0

Sample Description	#1		#2		#3		#4	
	Ash	Web	Ash	Web	Ash	Web	Ash	Web
1st Layer	0.0053	0.0733	0.0044	0.0650	0.0042	0.0675	0.0047	0.0681
2nd Layer	0.0058	0.0703	0.0045	0.0563	0.0053	0.0592	0.0047	0.0588
3rd Layer	0.0072	0.0807	0.0074	0.0880	0.0075	0.0802	0.0071	0.0808
4th Layer	0.0072	0.0814	0.0103	0.0996	0.0095	0.1035	0.0094	0.1049
Total	0.2555	0.3057	0.0265	0.3089	0.0265	0.3104	0.0269	0.3162

Table XII

The Distribution of Ash Using
Nalco 623 at pH 6.0

Sample Description	#1		#2		#3		#4	
	Ash	Web	Ash	Web	Ash	Web	Ash	Web
1st Layer	0.0047	0.0685	0.0040	0.0723	0.0045	0.0753	0.0042	0.0711
2nd Layer	0.0057	0.0742	0.0047	0.0567	0.0043	0.0573	0.0053	0.0580
3rd Layer	0.0061	0.0821	0.0075	0.0837	0.0072	0.0783	0.0077	0.0716
4th Layer	0.0096	0.0903	0.0099	0.1062	0.0094	0.1053	0.0099	0.1163
Total	0.0261	0.3151	0.0261	0.3189	0.0254	0.3162	0.0269	0.3170

Table XIII

The Distribution of Ash in a Standard Handsheet Using No Retention Aids at pH 6.0

Sample Description	#1		#2		#3		#4	
	Ash	Web	Ash	Web	Ash	Web	Ash	Web
1st Layer	0.0034	0.0067	0.0046	0.0724	0.0040	0.0827	0.0039	0.0811
2nd Layer	0.0052	0.0572	0.0054	0.0642	0.0053	0.0673	0.0057	0.0670
3rd Layer	0.0071	0.0828	0.0081	0.0844	0.0069	0.0708	0.0070	0.0698
4th Layer	0.0101	0.1053	0.0087	0.0970	0.0101	0.1002	0.0095	0.1013
Total	0.0258	0.3120	0.0268	0.3180	0.0263	0.3210	0.0261	0.3192

distribution between the two pH levels studied. At pH 5.5 the data in Table VII consistently contained less pigment than the standard data in Table XIII for the bottom layer. The top layer also compared favorably and indicated more pigment in this layer. However, when analyzing Cato 15 at pH 6.5 the data in Table VIII clearly indicated more pigment in the bottom layer than the standard samples. In fact these Cato 15 pH 6.5 samples are the most two-sided sheets with respect to filler distribution in the whole study. The comparison of Cato 15 at pH 5.5 and 6.5 was interesting with respect to optical efficiency. At pH 5.5 improvement in two-sidedness was observed while at pH 6.5 two-sidedness was increased, yet both pH levels maintained high opacities and scattering coefficients. This may indicate the types of titanium dioxide flocs formed by Cato 15 as a retention aid are conducive to greater light scattering than the flocs greated by the other retention aids. This may possibly be a function of the titanium dioxide within the floc itself rather than a function of the flocs relation to each other. This area however is not covered in this study as the evaluation of the pigment profile in the sheet is a study of the pigment flocs relationship to each other within the fiber web.

Natron 86 was not as clear cut in bearing out a trend. However, it is indicated from Tables IX and X, Natron 86 is similar to Cato 15. At pH 4.5 it appears there is more filler in the bottom level than at pH 6.5. Especially when samples 1 and 2 of pH 6.5 are considered. The top layer of Natron 86 pH 4.5 clearly does not have the filler content of the pH 6.5 samples. When Natron 85 samples are compared to the standards there is really no concrete evidence for improved uniformity. It also appears the pH 4.5 samples are more two-sided.

It was seen with Cato 15 and Natron 86 that differences in pH may cause changes in filler distribution. While Nalco 623 did not illustrate differences in pigment profile with respect to pH changes. The possibility of cellulose coflocculation with the titanium dioxide pigments may play a role in the differences of the pigment profiles at certain pH levels. It is interesting to note Cato 15 and Natron 86 are both cationic polymers. Nalco 623 is a anionic polymer.

It may be possible that cationic polymers have a greater tendency to flocculate cellulose at certain pH levels. While with anionic polymers flocculation with cellulose is not as pH dependent.

SUMMARY

In typing together the amount of retention, filler distribution and optical efficiency it can be seen that the retention aids with the higher retaining values were not the most optically efficient. It was also observed the optimum optical efficiency may not be at the level of optimum retention. The pH values chosen for the filler distribution study are the values where optical efficiency and percent retention is greatest for each retention aid. Only in the case of Nalco 623 did the highest optical efficiency fall with the optimum retention. This correlates with the theory that even filler distribution yields the highest optical efficiencies, since Nalco 623 was found to be an aid in evening the filler distribution at both pH 4.0 and 6.0.

Cato 15 showed a marked difference in filler distribution at the pH levels 5.5 and 6.5. At pH 6.5 there was a more even filler distribution then at pH 5.5 and this was the pH where maximum optical efficiency existed, despite a much lower filler content. This is also the point where the greatest optical efficiency existed in the filler distribution study when the amount of pigment was approximately the same as standard.

Natron 86 vs pH showed a difference between optical efficiency and optimum retention, but the reasons were not clear. Data for Cato 15 and Natron 86 indicate variables in retention vs. optical efficiency exist at certain pH levels that do not exist with Nalco 623. One

possibility that bears mentioning is that flocculation with cellulose may be a more critical factor with cationic retention aids than with anionic retention aids at certain pH levels.

CONCLUSIONS

The conclusions from this study are as follows:

1. The percent retention due to the retention aids studied was greatly influenced by the pH at the time of sheet formation. The pH values where the optimum retention existed for Cato 15, Natron 86 and Nalco 623 were approximately 5.5, 4.5 and 6.0 respectively.
2. The optimum optical efficiencies as measured by the scattering coefficient did not generally exist at the pH levels where retention was optimum.
3. For a given amount of titanium dioxide in a sheet, the greatest optical efficiencies were gained without the use of a retention aid. It was also found the retention aid, Cato 15, that produced the lowest retention produced the greatest optical efficiency. It was shown, however, that Nalco 623 produced equivalent scattering coefficient with Natron 86. Nalco 623 did have the greatest retention values and the best filler distribution profile in the sheet.
4. Nalco 623 proved to be an aid in reducing two-sidedness at both pH 6.0 and 4.0. It's pH values for optimum retention and scattering coefficients respectively.

5. In the case of Cato 15, it was determined a retention aid can be of value in filler distribution at one pH and offer no improvements or even impede filler distribution at another pH. Natron 86 also indicated this effect.
6. The retention aids ranked as follows in the maximum amount of fillers retained: (1) Nalco 623, (2) Natron 86 and (3) Cato 15. However, optical efficiency was ranked the order of Cato 15 as the highest with Natron 86 and Nalco 623 approximately equivalent.

SUGGESTIONS FOR FURTHER WORK

The experimental data has indicated the pH levels where the retention aids yield optimum retention and optimum scattering coefficients. The pH values for these optimum conditions could be more accurately defined by additional work evaluating smaller pH increments. This experimental work should be focused around the pH levels determined to yield maximum results. The work to define these pH values should be directly patterned after the experimental procedure which determines the optimum pH levels.

It would also be interesting to determine the effect of pH on retention and scattering coefficient when combinations of retention aids are used. Again this could be patterned after the work in this thesis. The effect of combinations of retention aids on the pigment profile throughout the sheet is another topic which would be of value to study. The Beloit Sheet Splitter is an excellent tool for this type of work.

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