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The Effect of Poly-Aluminum Silicate Sulfate Retention of Colored Papers

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A Thesis submitted
in partial fulfillment of
the course requirements for
The Bachelor of Science Degree

Department of Paper Science and Engineering
Western Michigan University
Kalamazoo, Michigan
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ABSTRACT

The purpose of this thesis experiment was to study the effect of Poly-Aluminum Silicate Sulfate (PASS) on the retention of colored papers. This was performed to reduce the usage of Melamine Formaldehyde based retention aids due to their negative environmental impacts as well as to reduce the usage of Sodium Aluminate, a cationic additive and pH buffer, due to its negative fade impact on colored papers.

This was accomplished using PASS as the retention aid mechanism and caustic soda as well as soda ash as pH buffers and cationic additives. Paper was made under alkaline conditions. Colored pigments were utilized to accomplish a critical color match.

This study has shown that by using the PASS product instead of the Melamine Formaldehyde/Sodium Aluminate combination that increased britt jar retention, higher first pass retention on the papermachine, increased fade resistance, improved cost efficiency, and better environmental aspects were achieved.

The retention studies were performed with the dynamic drainage jar (britt jar) and the papermachine at Simpson Paper Company in Vicksburg, Michigan. Retention values improved for the papermachine study as compared to the laboratory setting.

Color-matching values were determined using the FMC-II method which is very similar in measurement technique to the I.a.b. values determined directly by the computer. Fade values were determined using a weatherometer.

ACKNOWLEDGEMENTS

I would like to take this opportunity to thank the people that made this project possible, for without them it would have been much more difficult.

I would like to express my gratitude to Mr. Charles Dickens, Jr., my industry advisor from Simpson Paper Company, for all of his patience and helpful insight. With his constant encouragement and guidance this thesis was successfully completed.

Thank you to Mr. Richard Flores for your guidance through the first two semesters of this project. I appreciate Dr. Ellsworth Shriver for picking up me and my project last minute after Mr. Flores retired. You both have definitely been a great encouragement to me.

Last, but not least, thank you to Mr. Bill Poure from General Alum and Chemical Company for all of your helpful advice pertaining to this new chemical your company supplies.

INTRODUCTION

A thorough investigation of the effect of Poly-Aluminum Silicate Sulfate (PASS) on the retention of colored papers necessitates a complete understanding of the areas of retention as well as that of the color I.a.b. system. A description of the PASS product is also very crucial in determining these retention effects.

PASS AS A RETENTION AID

Poly-Aluminum Silicate Sulfate (PASS) is a new chemical that was designed as a retention aid as well as a coagulant/flocculant. It has just been introduced onto the market within the past few years and had not previously been tested on colored papers. I have used this PASS product as a retention aid.

PASS is a new chemical that has a specially formulated, basic Aluminum salt that contains a very reactive polymeric aluminum Silicate Sulfate. PASS when used as a retention aid produces a large, non-aggressive, non-corrosive, polymeric floc that will not break up completely with hydrodynamic shear. It hydrolyzes directly when it comes in contact with water therefore it is important to add it the latest in the process as possible.(1) A unique characteristic of this new chemical is that it will break up partially with shear but it also will reaggregate after turbulence decreases. That is one main reason why it is so effective on the papermachine as a retention aid. When white water

is recirculated, it brings more PASS product that has reagglomerated back into the stream to improve retention. The PASS chemical attracts the small fines and pigments and attaches itself to the longer fibers therefore improving the retention on the papermachine.

RETENTION DEFINED

In the modern papermaking industry, cost efficiency of any process is the most crucial way to improve the performance of any mill. Retention, although it is one of the least understood areas of the papermachine, can be one of the best ways to utilize an economically rewarding process.

A very physiochemical problem found in the paper industry today has been found to be the retention of fibers and cellulosic fines and other colloidal particles present in the furnish such as rosin size, latex emulsion, starch, dry strength additives and filler pigment.(2) This retention can be defined as holding these various additives in the moving web which will compose the final sheet of paper. Improved retention is required to produce better quality paper with fewer losses of raw materials that will in turn increase the ability to reuse the water within the mill. By improving the retention a reduction in the BOD loads in the mill effluent can also occur. This will produce fewer chemical deposits in the headbox, stock lines, wire pit, seal pit and the save-all surfaces which could decrease the efficiency of the system.

FIRST PASS VS. OVERALL RETENTION

There are two ways to perceive retention. One is to minimize or ignore the first pass retention and depend on the white water recirculation to improve the overall retention. The other is to improve the performance of the first pass retention by adding chemicals to the area in the process that is losing raw materials. Retention can therefore be expressed as either first pass or overall retention which include retention of total suspended solids, ash and cellulosic fines. (3) Retention occurs in several ways and these will be discussed throughout this report.

First pass retention, or single pass retention, is known as the amount of a substance, which includes total suspended solids, ash, and cellulosic fines, that will remain in the completed sheet as compared to the amount that is entered onto the papermaking wire from the headbox. The percentage first pass retention varies between machines and is crucial in optimizing papermaking operations. There are two key components that influence the first pass retention. One is the mechanical entrapment of fine particles in the forming web. The other is the colloidal attraction forces between the dispersed solids of the stock that depend on the chemical additives. The performance on the paper machine is a resultant of these two characteristics.

The first pass retention is determined by calculating the consistencies from both the headbox and the tray water. While the ash determination of the sheet is obtained by dividing the sheet ash by the headbox ash content. Both aid in the evaluation of the

retention aid. One factor impressed upon by Waddell (4) is the location of the white water tray sampling point for first pass retention. This point must remain constant for each particular paper machine and is difficult to determine a comparison between two different machines. Frankle and Sheridan (5) have developed an easy, effective method for determining first pass retention. They related the retention to the sewer losses. They included the cleaners, screens, and save-alls to determine the efficiency and showed that these losses are proportional to the load on the save-all. As the losses are increased, a decrease in retention will result.

The overall retention can be described as the amount of material remaining in the completed sheet compared to the amount of material that has been added in the process all together. This includes all material in the stuff box and beater rooms as well. Waddell stated that the overall retention refers to the general efficiency for longer period and includes the losses to the sewer from the savealls. It relates the materials purchases vs. all the fibers and fillers converted to saleable paper and broke.

MECHANISMS OF RETENTION

The papermaking system has many complicated mechanisms used for bringing about retention. Several of the authors have investigated these mechanisms which include mechanical filtration, mechanical attachment, physiochemical- charge attraction, physiochemical- co-flocculation, bridging, and the patch model.

Many outside factors affect these mechanisms. Most times, a combination of a few of these mechanisms are used in conjunction with one another to achieve better retainment. These mechanisms are discussed in further detail in the following few pages.

Mechanical Filtration

The papermachine consists of a headbox and a forming wire in which the surface is created for the sheet of paper. As the pulp stock is forced onto the wire via the headbox, the long fiber part of the stock is trapped on top of the wire and held in place. The particles that are too small to be filtered out by the wire mesh pass through the wire and are lost in the white water below. This filtering of the filler and small fines particles gradually decreases as the fiber mat forms and builds up.

Chemicals are added to the stock furnish that help these fines and filler particles to be flocculated or coagulated onto the longer fiber particles that traps them on top the fiber mat. The chemical that is added will change the flocculation or coagulation of the small particles. PASS is one such chemical that is a coagulant and flocculant as well as a retention aid. There are both kinds of retention aids. PASS happens to have both characteristics. The coagulation and flocculation can be distinguished by LeMer and Healy in the following manner. Coagulation is the "driving together" of the particles to form a tightly knit group. Flocculation is the process of creating "loose fibrous structure". It is described in a PASS bulletin(7) as a destabilization of colloids (coagulation) which is brought about by

neutralizing the charge that keeps the colloids apart. It is accomplished by the PASS chemical with the use of aluminum salts. The stage that allows the colloids to adsorb into a fast settling floc or to agglomerate is the floc forming stage or the flocculation. In the pores of the fiber mat formed on the papermachine wire, the filtration process takes place.

Mechanical Attachment

The mechanism of mechanical attachment is described by Fraik(8) as the process by which the filler and/or fine particles become lodged or entrapped on the fibrils and imperfections of the fibers and retained fines. The theory of mechanical attachment is classified as media filtration.(9) The retention of these particles is achieved during the filtration by the internal forming structure of the filter media. Both the pores of the web and the fibrils of the fibers and fines are included in this.

The filtration of the media is dependant on many papermaking parameters. The basis weight increases the retention through the mechanism of pore filtration. Retention can be increased with more refining because of mechanical attachment. By decreasing the speed of the machine and reducing the suction box vacuum, an increase in retention because of mechanical purposes will occur. All of these parameters and many others can be changed to affect the retention of the papermachine.

Physiochemical — Charge Attraction

A difference in the electrokinetic charge exists between the cellulose fibers and the filler which attracts them to one another.(10) Charge attraction occurs between these two oppositely charged particles to bring them together. They tend to attract one another and form a floc that will be retained more easily. This does not occur very frequently in the papermaking process unless an agent is provided that will chemically alter the prevalent electrical charge of the system. The fiber, filler, and fines portions carry the negative (anionic) charge and will tend to repel one another and are only attracted to one another with the usage of a positively charged (cationic) chemical additive.(11)

An attraction occurs between the cationic agent and the cellulosic fibers when a cationic agent is dispersed in the system. If a filler such as titanium dioxide is dispersed with a cationic agent, an attraction will become present between the cationic additive and the titanium dioxide.(12)

Physiochemical — Co-flocculation

In the ~~absence~~ of electrokinetic charges on the individual particles, flocculation can occur. Factors that effect this flocculation include things such as pH and shear. The required electrokinetic condition for flocculation is enhanced by the addition of a chemical retention aid that will suppress the electrical double layer and allow the materials to floc. The colloidal forces formed available with use of a retention aid may or may not be resistant to shear.

There are three factors which affect the co-flocculation: the collisions encountered in the system, the aggregate formation, and the aggregate strength.(13)

Bridging

Bridging can be defined as the mechanism by which a long chain polymer forms a connection between two or more particles. This connection can be made between the fibers and the pigment particles, between cellulose fines and fillers, between two pigment particles, or even between two fibers. Lemer and Healy(14) have proposed two types of bridging that are most prevalent. These types are demonstrated in figure 1 below.

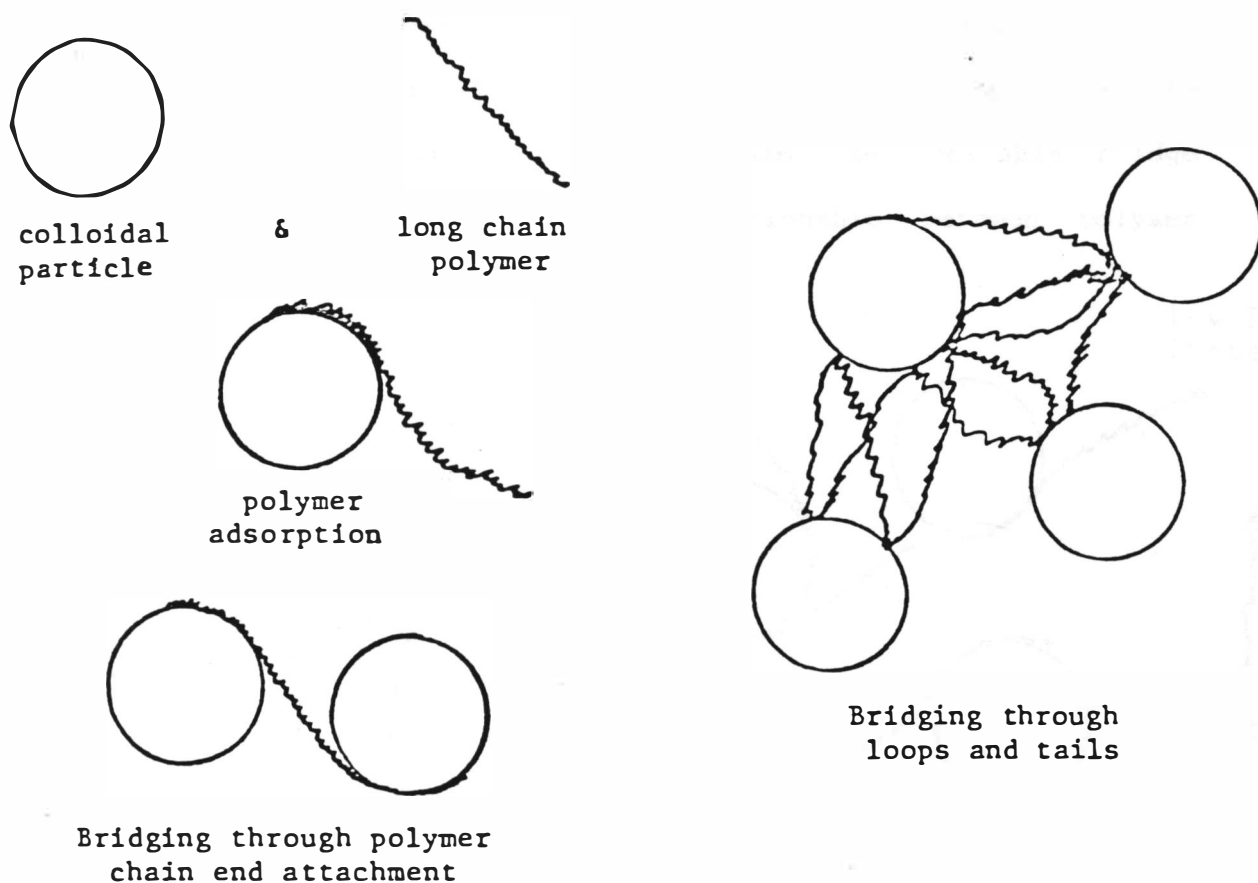


Figure 1

Bridging can occur when one end of the same chain attaches to one particle, while the other end of the same chain attaches to another particle. Bridging through loops and tails are involved in the second method. A long chain polymer adsorbs on the particle surface at different places along this chain. The remaining portions which are unattached extend out into the solution and are ready to form bonds with the other available particles.

The bridging gives the flocs increased shear stability. The portion of attachment must be strong. It has been suggested by Britt(15) that the preadsorption of a small, highly cationic molecule provides the correct conditions for proper bridging to occur.

Too little polymer will leave available bridging sites unoccupied. Too much polymer will prove to cause coating of the particle surfaces and therefore ~~decrease~~ the available bridge sites. Figure two shows the relationship between polymer concentration and available bridge sites.

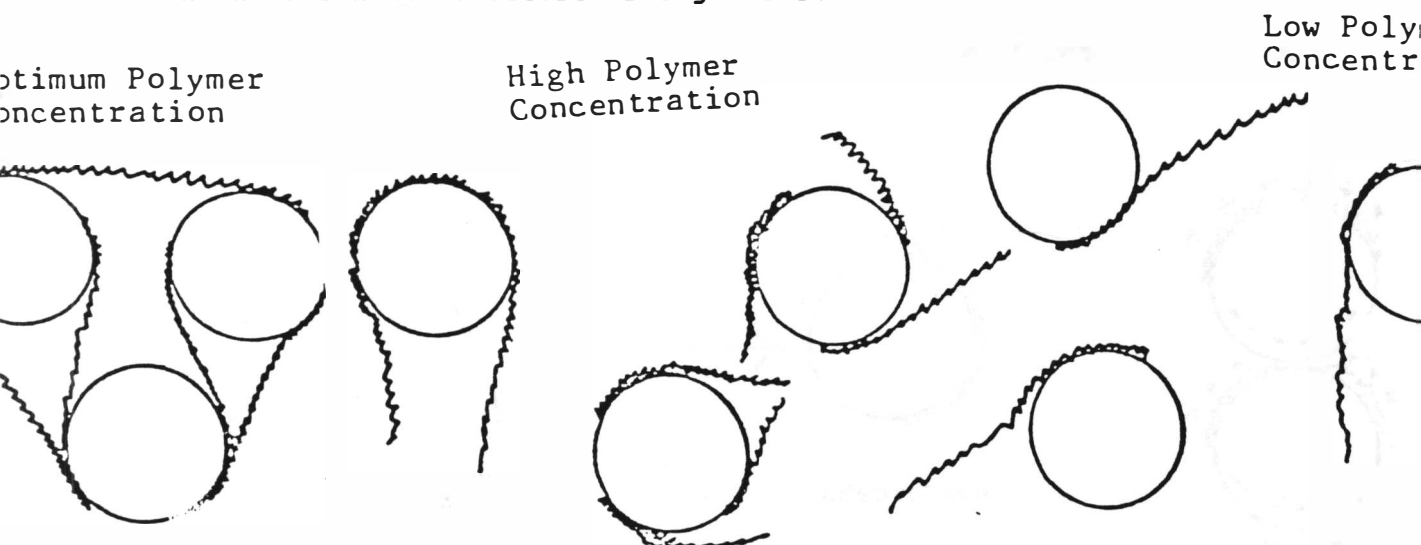
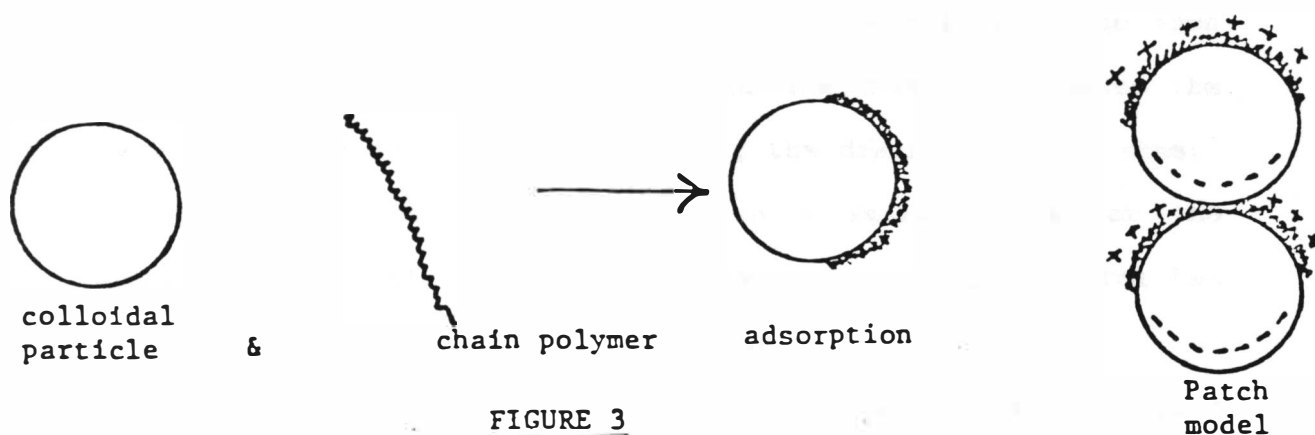


Figure 2

The mechanism of bridging can form hard or soft flocs. This is dependant on the turbulence, time duration, and intensity of the applied shear. Hard flocs resist a break down in their structure due to turbulence. They do not reform. Soft flocs will reaggregate when applied shear is removed. A study performed by Swanson(16) shows that shear resistance of the floc formed by a charged particle is independent of the molecular weight of the polymer. He also discovered that soft flocs formed by high molecular weight polymers tend to reform rapidly after excessive agitation is removed.

Patch Model

The last retention mechanism is called the patch model. According the Goossens and Luner(17) partial neutralization of the particles by adsorption of a small, cationic polymer is necessary for patching to occur. For coagulation to occur, Van der Waals forces of attraction between positive and negative sites on the particles becomes the driving force. Figure three is a good demonstration of this phenomenon.



FACTORS THAT INFLUENCE RETENTION

Many parameters are important in the retention of paper. These factors are included in the beater room before the stock gets to the wire, some are inherent on the papermachine forming wire, and still other factors are active with the materials and equipment with which the paper is made.

Many of these factors that effect the retention are listed below. A primary concern in the papermaking industry is the surface area and accessibility of the cellulose to the retention aid. The temperature, pH, shear, zeta potential, polymer size, bonding ability, and freeness are all parameters which must be considered.

Temperature

The physical and chemical properties of the papermaking system are affected by the temperature of the system. It affects the fiber, water, retention aids, and other additives, which all affect the retention of the system.

The surface area of the cellulose fibers will decrease when heat is applied to the system. Higher temperature decreases the viscosity of the system thus increasing the drainage of the sheet. An increase in temperature results in a smaller area for the retention aid to act upon. The negative charge that the fiber has will possess a smaller net charge density.

There is more flocculation and higher retention with increased temperature because the net charge density of the polymer

decreases. The surface charge density will increase which means the repulsive forces decrease and flocculation is increased. Changes in electrokinetic properties occur due to an increase in temperature as well.

pH

For the particular grade of paper that this thesis is about the pH range of the system was required to be between 7.5-8.5. This paper is a decorative lamative paper that is used commercially as a backing around a picture frame. Alkaline conditions are required to reduce the fade of the paper and to increase the life of the paper.

In the past it was expected to run the paper machine at pH ranges of 4-6 due to the presence of various electrolytes. The higher the pH, the more electro-negative the fiber becomes. This is the main reason that in alkaline papermaking conditions that a reduction in retention occurs. I personally have not seen this in this experiment as retention values of up to 96% were obtained.

Shear

Turbulence in the headbox is created and forces a hydrodynamic shear to occur between fibers and filler that will reduce the retention on the papermachine. The fan pump is another area of high turbulent flow in which shear is common. In areas of high shear, the flocculated filler and fines particles are removed or deflocculated due to the shear forces. With soft flocs, this deflocculation will reagglomerate after removing the shear. With

hard flocs, reagglomeration will not take place. Shear is required for proper sheet formation, and a balance between the retention and the correct amount of shear must be determined.

Zeta Potential

Zeta potential is a complicated mechanism. It is the electrokinetic potential or the potential developed between the fixed, absorbed ions on a particle and the ones that remain in solution. A good representation of this potential is shown below in figure 4.

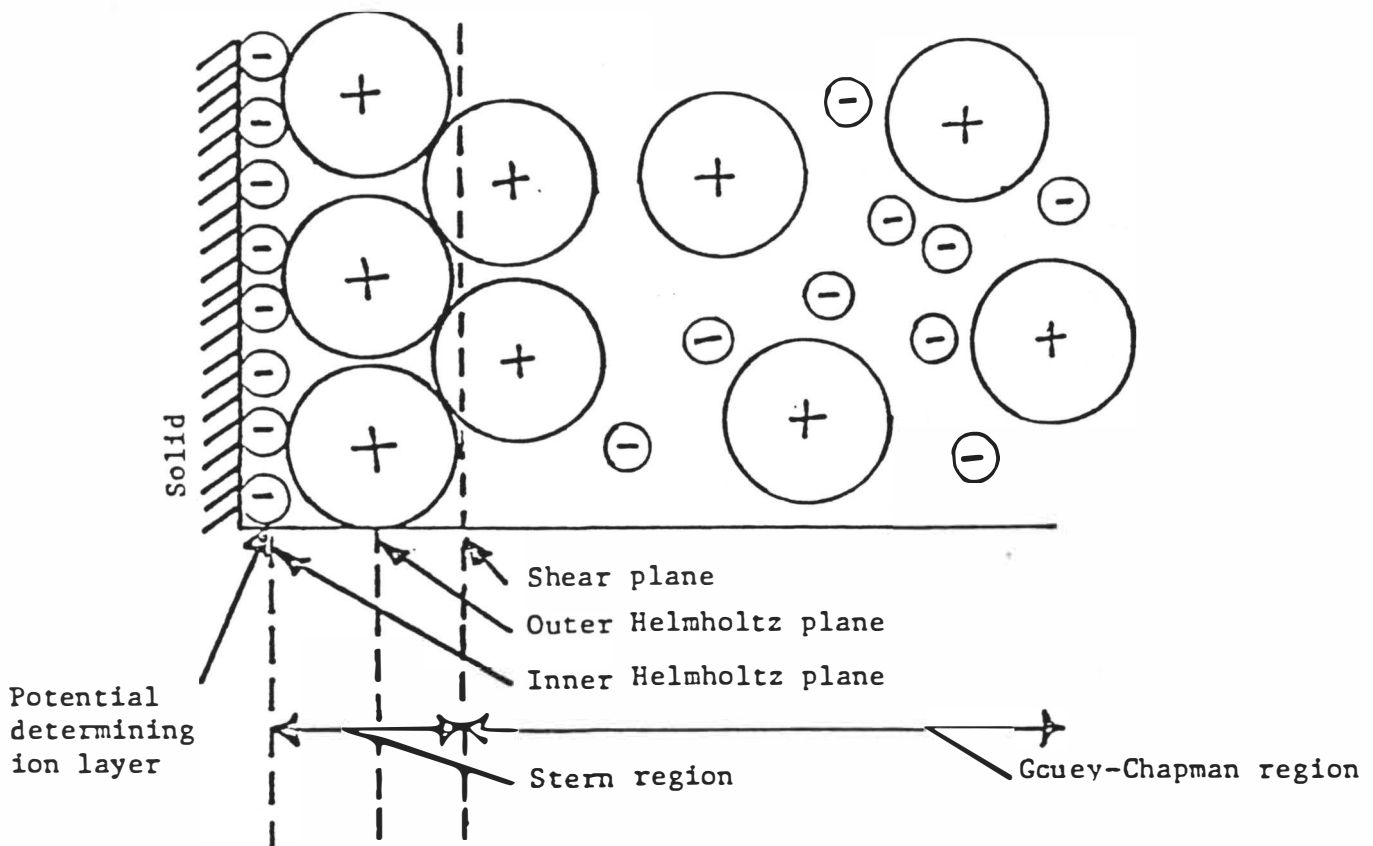


Figure 4

This figure was taken from an article by Williams and Swanson(19) and is the best demonstration of the electrical double layer that I have found. It shows the adsorbed ions and counter ions. The potential developed at the interface between the Stern region and the Gouey Chapman region is labeled the zeta potential. This zeta potential is an indication of the state of the electrical double layer. As the electrical layer becomes more suppressed, the zeta potential decreases upon addition of a chemical agent. As the zeta potential approaches zero, the electrical double layer is totally suppressed. At this point the flocculation and coagulation occur rapidly.

Refining

The hydrodynamic surface area of the cellulosic fiber increases as the stock is increasingly refined. This increases the fines fraction in the furnish as well. The additional exposed fibrils tend to increase the retention due to mechanical entrapment. The fines will adsorb filler and additive particles. By increasing the refining, the freeness of the stock decreases. The increased surface area of the fibers is the one reason that the cationic demand increases because it also increases the amount of carboxyl groups that have been exposed. This is what will determine the charge of the system. With increasing the amount of refining, the inaccessible regions inside the fiber are opened up which will in turn increase the cationic demand.

RETENTION AIDS

Retention aids as presented by Nelson and Jursich(20) are defined as any chemical that is able to flocculate, coagulate, or change the surface characteristics of the fibers and other particles, or which can act as a chemical bridge between particles of a like charge. The four classes of retention aids they describe are:

- 1) Inorganic compounds - including alum, sodium aluminate and activated silica.
- 2) Naturally occurring organic compounds - glues and starches
- 3) Modified natural organic compounds - modified gums and starches
- 4) Synthetic organic compounds - cationic, nonionic, and anionic water soluble organic compounds.

One of the oldest retention aids used today is alum. It reduces the pH therefore decreasing the electron activity of the fibers and inducing the flocculation.

MEASURE OF RETENTION

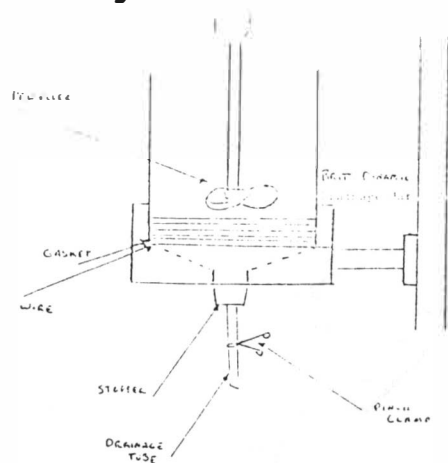
Over the years there have been many ways to test the retention of the paper. The oldest is the hand sheet analysis. It unfortunately does not incur shear and is performed at a high dilution rate.

A method that has been incorporated into this experiment and has found to be quite useful is the dynamic drainage jar.

Otherwise known as the Britt Jar, the dynamic drainage jar incorporates turbulence in the flow that creates hydrodynamic shear at a low dilution.

The dynamic drainage jar is made of durable plastic with side baffles. At the bottom of the plastic cylinder is a one inch diameter hole for free drainage. A 200 wire mesh wire is supported between the bottom of the cylinder and the hole. This configuration will allow for drainage through the wire during testing. there is a 1 1/2 inch propeller about 1/8 inch from the bottom of the jar that is driven by a variable speed motor. Figure 5 demonstrates this configuration.

Figure 5

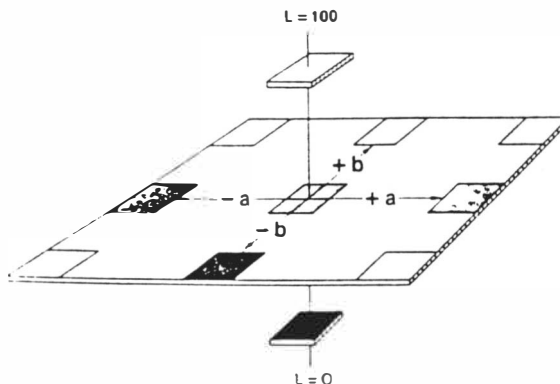


The bottom hole is first plugged to keep drainage from occurring until the sample has been treated according to the desired conditions. The pulp slurry sample is then added and the motor started. The propeller provides shear and its speed may be varied to provide the desired speed necessary to correlate to an actual papermachine. The propeller causes turbulence which prevents a mat from forming on the wire. This will allow the ~~researcher~~ to determine retention values caused by physiochemical interactions alone, not affected by mechanical filtration caused by

a forming mat. the sample is drawn off the bottom of the jar through the hole. By extracting samples over set time span, the drainage rate can also be calculated.

COLOR MEASUREMENT

Color measurement in this experiment was determined by the MacBeth Color Computer that analyzes both L.a.b. and FMCII color measurements. The lab system follows the CIELAB color space diagram as is shown in figure 6 below.



The values of L, a, and b are determined by the tristimulus values, X, Y, and Z as shown below:

$$L^* = 116 \left[\frac{Y}{Y_n} \right]^{1/3} - 16$$

$$a^* = 500 \left[\left[\frac{X}{X_n} \right]^{1/3} - \left[\frac{Y}{Y_n} \right]^{1/3} \right]$$

$$b^* = 200 \left[\left[\frac{Y}{Y_n} \right]^{1/3} - \left[\frac{Z}{Z_n} \right]^{1/3} \right]$$

DL, Da, Db, and DE values are determined by difference between the sample and a standard known sample.

$$DEab = [DL^2 + Da^2 + Db^2]^{1/2}$$

The values of DL, Da, and Db are shown below:

| | + | - |
|-------|----------------|----------------|
| DL* | lighter | darker |
| Da* | redder | greener |
| Db* | yellower | bluer |
| DCab* | more chromatic | less chromatic |
| DHab* | + hue shift | - hue shift |

On each sample the computer will average three readings and record an average of these readings which is shown in the data to this experiment.

PROBLEM STATEMENT

The purpose of this experiment was to eliminate the use of melamine formaldehyde based retention aids on colored papers because of the increased government regulation. This experiment was also to determine a replacement for sodium aluminate, a cationic additive and pH stabilizer, due to its negative impact on fade-resistance. A new chemical recently developed by General Alum and Chemical Company called Poly-Aluminum Silicate Sulfate (PASS)

claims to have better retention, to increase the filler retention of the sheet, to improve efficiency of the process, to reduce effluent solids, and to be more cost efficient.

EXPERIMENTAL DESIGN

Laboratory Experiments:

- 1) Control: Melamine-Formaldehyde/Sodium Aluminate
- 2) Caustic Soda Alone
- 3) PASS with Caustic Soda
- 4) Soda Ash Alone
- 5) PASS with Soda Ash

Control Parameters:

- 1) 50/50 HW/SW blend for furnish
- 2) Run under alkaline conditions
- 3) Refined stock to 300 CSF
- 4) Controlled amount of Calcium Carbonate filler
- 5) Controlled amount of colored pigment

In the lab I was trying to determine the optimum level of addition rate for the PASS product. I varied the amount of the PASS product and used the caustic soda and soda ash only as pH stabilizers and cationic additives to achieve a pH of approximately (7.5-8.5). Handsheets were made on the Noble and Wood handsheet apparatus. Britt jar retention values were determined for each experiment.

After compiling the data from the sheets that received the critical color matches, I then chose the best combination of the PASS product to use on a papermachine trial that was later performed at Simpson Paper Company in Vicksburg, Michigan.

PROCEDURE

Britt Jar Retention:

Retention by use of the Britt Jar necessitates a fractionation procedure, Calculations, and Retention determination. These procedures are discussed in below.

Fractionation:

For the fractionation procedure, a sample of stock to be tested is adjusted to a consistency of 0.1%. It is important to know the consistency exactly. It is ~~recommended~~ that the sample be stirred continuously in a suitable container. A 500 ml sample of this 0.1% consistency stock is placed in the jar which contains a 200 mesh screen. The agitator is turned on up to 1500 rpm for a few seconds for complete dispersion, then down to 750 rpm. The bottom orifice is opened and drainage is caught in a 2000 ml beaker. Wash water is prepared containing 0.01% TSPP, 0.01% Dispex N-40 (at 40% solids), and 0.01% Sodium Carbonate. After drainage is complete, 500 ml of wash water is poured into the jar (bottom closed), stirred, and drained as before. This is repeated until there is 2000 ml in the catch beaker. This contains the fines fraction. A 500 ml sample of water is now poured into the jar and allowed to drain into a clean glass beaker. This filtrate is

observed for clarity and should contain no appreciable amount of suspended matter. The residue of the fiber on the screen is transferred to a weighted filter paper on a Buchner, dried, and weighed.

Calculations:

If the sample is exactly 0.1% consistency, the 500 ml volume contains 500 mg of suspended solids. This value must be known exactly, say within 1-2 mg. Let's say that the total solids was 514 mg and the residue of fiber filtered out was 380 mg. Then the fines fraction is $514 - 380 = 134$ mg or 26.0%. Note that the fines fraction contains both pulp-derived organic fines and mineral filler.

Retention:

The first step in the determination of retention of fines in a paper stock sample is the fractionation procedure described above.

For the retention test, a 500 ml sample of stock to be tested is placed in the jar with the bottom outlet hole stoppered. The consistency of this stock is at 0.5%. The stopper carries a short glass tube 5/16" O.D. connected with a rubber tube with a pinch clamp to a typical medicine dropper. The purpose of this arrangement is to restrict the flow during the test so that the screen remains free and open during the test. At high degrees of turbulence, the screen remains clean regardless of rate of flow, but at low turbulence a clean screen requires a flow rate restricted to about 100 ml/30 sec.

Calculations:

The 500 ml sample placed in the jar was measured in a graduated cylinder. Suppose that the consistency was determined to be 0.517%, then the total solids in that sample would be $500 \times 0.517 = 2.585$ g or 2585 mg. Suppose that the % fines/filler as determined by the fractionation was 29%, then the total fines/filler in the sample would be $2585 \times 0.29 = 750$. Now suppose that the weight of the aliquot filtrate was 102.5 g and the solids in that sample was 85 mg; then the percent retention of the fines/filler fraction would be:

$$\text{Unretained: } \frac{85 \times (500/102.5)}{750} \times 100 = 55.3$$

$$\text{Percent Retention (based on fines/filler)} = 100 - 55.3 = 44.7\%$$

Colormatching:

In this experiment the optimization of the PASS product's flow rate was the main concern in receiving a critical color match. On this particular grade of paper an, FMC II color reading, which is approximately three times the L.a.b. value discussed earlier in this report, is required to be under 2.0 total delta E. Colormatching is science in itself that requires a lot of trial and error of pigment addition. When a negative DL value is high but the rest of the values are quite low, it is certain that the color is pretty good but the depth of the sheet must be adjusted because the sheet overall is too light. Colormatching is performed by using the MacBeth color computer. The starch which coated this paper was made up to the specifications of the actual papermaking

process. The starch consisted of a cationic starch mixture containing some wax.

Base Stock Preparation:

The base stock that was utilized in this experiment was a 50/50 hardwood/softwood furnish that was beaten in a valley beater for approximately one half hour. The ending freeness was 300 CSF which is a requirement for this grade of paper. All procedures were performed to TAPPI Standards.

Order of Addition:

The materials for the color match and retention tests were added in the following sequence: Stock, Titanium Dioxide, Calcium Carbonate, Dispersant, Colored pigments, caustic or soda ash, and finally PASS.

RESULTS

The following results and conclusions were obtained from this experiment. Higher Britt Jar Retention in the lab and increased First Pass Retention values were obtained on the papermachine. There was a fade-resistance increase of approximately two-fold, better environmental characteristics were observed, and a cost efficiency was utilized.

Experiment #1-Melamine:

In the first experiment the purpose was to use it as a control against which the other four experiments could be run. It took five tries to receive a proper critical color match as can be

observed by the chart and graph in the results appendices 1. I was able to obtain a color match under 2 FMC II units as is a set specification on this particular grade of paper. A match was obtained with a DE value of 1.26 which is definitely within the 2 unit critical range. Retention values for the Britt Jar analysis which are comparable to the machine speed on the paper machine are between 84 and 82. This is low compared to 90 and 89 percent retention with using the PASS product. The melamine changed the color of the paper with fade by 3.214 units off from the standard where the PASS product averaged around 1.8 units.

Caustic Soda vs. Soda Ash:

Very poor retention results were obtained by using only caustic soda and by using only soda ash. The mechanism that holds the small fines and filler particles in the sheet is a form of alum. There was no form of alum present in these processes therefore it is shown in the Results Appendices 2 and 4. The DE value was in the fifties for both when compared to the standard which should remain under 2 units. Overall, these two experiments were failures.

PASS with Caustic Soda:

Tremendous results were obtained by using the PASS chemical with caustic soda. Britt Jar retention values increased by 5-8%. Paper machine retention was approximately 97% as compared to 87% for melamine formaldehyde/sodium aluminate. Color matches were obtained within the 2 unit FMC II range and overall it is more environmentally friendly than the melamine. It took a while to find a color match because the PASS product retains approximately

40% more calcium carbonate in the sheet than the melamine thus making a lighter sheet. A determination of the amount of calcium carbonate reduction was determined by using 100% of the PASS product as compared to the melamine. By using the full amount of PASS in the lab a reduction of 40% calcium carbonate could be obtained as is prevalent in the 3rd results appendix. It was also determined that by using 50% of the PASS in the lab that a color match could be obtained utilizing 100% of the normal calcium carbonate. This gave the best cost results as the PASS product is more expensive than the calcium carbonate filler.

PASS with Soda Ash:

Very similar results were obtained using the soda ash in place of the caustic soda. Slightly lower retention values of 2% were found but overall it was very impressive and because soda ash costs less than the caustic soda it was determined to use it on the papermachine trial.

Papermachine Trial:

A papermachine trial was conducted at Simpson Paper Company in Vicksburg to determine a correlation between the lab and the actual process. Half of the machine run was conducted using the melamine and the other half was performed using the PASS product with soda ash as a pH stabilizer. Tremendous reduction in the flow rate of the PASS product was observed to obtain similar color on the machine. One tenth the rate of the PASS was used as compared to the melamine. Retention values on the machine were 10% higher for PASS. Approximately 10% more colored pigment had to be used to obtain a color match. Roughly 5% more starch was used as well.

Because of the mechanism of the PASS product, it hydrolyzes as soon as it hits water therefore it was added just before the headbox for best results. The reason it received so much less flow rate on the machine than in the lab are because in the lab the sample is much more dilute causing more hydrolysis to occur, secondly because on the paper machine the white water is recirculated. The PASS chemical reagglomerates when shear is removed therefore increasing the action of the chemical the second time around. Melamine is also a wet strength additive that is partially the reason it doesn't pick up as much starch as the PASS will. Overall, the cost reduction by using the PASS product is half the cost of the retention aid, with no use of sodium aluminate it is considered to be a significant cost attainment, the added cost of the colored pigment along with the cost of the soda ash are the only added cost figures. Overall, a cost savings of 5% within the process is obtained by using this product which can calculate to a significant amount when you consider tonnage of paper produced. Fade resistance improved similarly to the lab results by 1.729 DE units for PASS compared with 3.302 DE units for melamine.

CONCLUSIONS

In this study it was determined that by replacing the melamine formaldehyde/ sodium aluminate combination for a retention aid with Poly-Aluminum Silicate Sulfate that many significant results were obtained. The calcium carbonate retention was increased by 40%. Britt jar retention increased, first pass retention improved on the paper machine, increased fade resistance was achieved, overall cost efficiency improved, and better environmental aspects were attained. It was a very successful experiment that took a lot of time and was well worth it.

RECOMMENDATIONS

Due to the positive aspects of this product on the retention of colored papers, it is my recommendation that this product be tried on other colors for their pigment retention. This experiment was run on a light pink color. It may have some different affects on a deep purple or a bright red.

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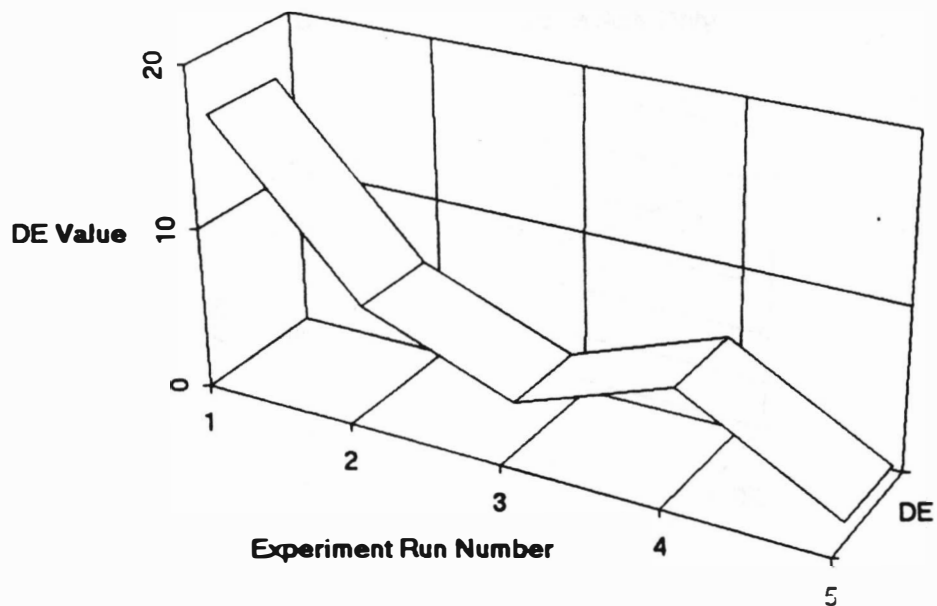
RESULTS APPENDICES 1-5

(1)

Melamine Formaldehyde/ Sodium Aluminate

| Sample # | 1 | 2 | 3 | 4 | 5 |
|-----------|--------|------------|---------------|---------------|---------------|
| DL | | | | | -0.4 |
| Da | | | | | -0.12 |
| Db | | | | | -0.348 |
| DE | 16.421 | 6.68 | 3.11 | 6.6 | 1.26 |
| What did? | | 20%red add | 25% red add | 22%red add | 25%red add |
| | | | 5% yellow add | 8% yellow add | 8% yellow add |

Color Values For Melamine



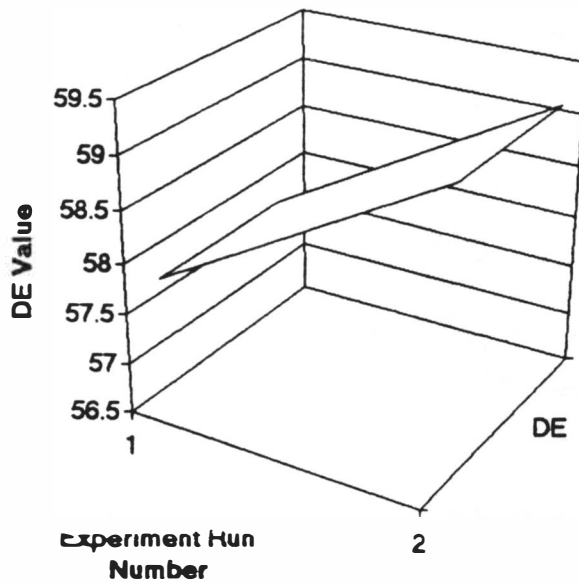
□ DE

(2)

Experiments #2 #4

| Sample # | Caustic Only | Soda Ash Only |
|----------|--------------|---------------|
| DL | | |
| Da | | |
| Db | | |
| DE | 57.65 | 59.25 |

Caustic Only vs. Soda Ash Only



(3)

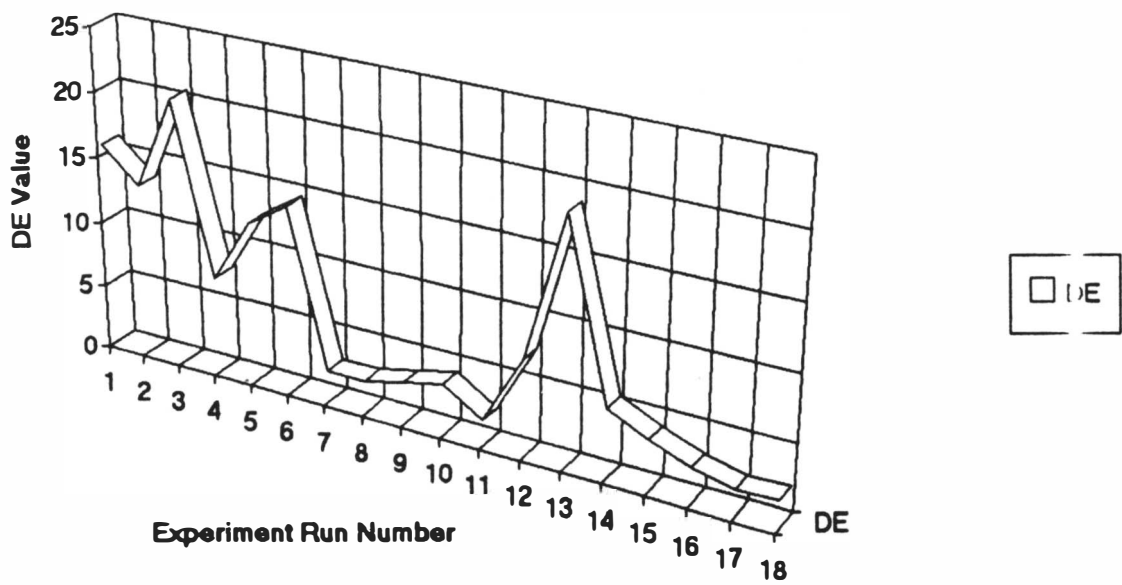
Experiments #3 #5

| Sample # | 1 | 2 | 3 | 4 | 5 | 6 |
|-----------------------------|--------|--------|--------|--------|--------|---------|
| DL | 13.454 | 11.064 | 18.969 | -4.887 | 4.83 | 6.635 |
| Da | | | | 5.32 | -11.52 | -12.815 |
| Db | | | | 2.066 | 0.042 | -0.483 |
| DE | 16.85 | 13.321 | 20.521 | 7.513 | 12.5 | 14.439 |
| %PASS | 59% | 50% | 100% | 100% | 100% | 100% |
| %CaCO ₃ | 100% | 100% | 100% | 50% | 62% | 70% |
| %CaCO ₃ in Sheet | 1.2 | 1.03 | 3 | 0.9 | 1.2 | 1.6 |
| | | | | | | |
| | | | | | | |

| 7 | 8 | 9 | 10 | 11 | 12 | 13 |
|--------|---------------|----------------|------------------|---------------------|--------|---------|
| -0.542 | 0.052 | -2.132 | -0.069 | -0.152 | 4.46 | -11.443 |
| 0.32 | -0.173 | 0.907 | 3.801 | 1.527 | -4.37 | -6.928 |
| -2.42 | -2.534 | -2.0239 | -1.002 | -0.998 | -3.927 | 13.377 |
| 2.5 | 2.541 | 3.221 | 3.931 | 1.98 | 7.376 | 18.761 |
| 100% | 100% | 100% | 100% | 100% | 50% | 50% |
| 60% | 60% | 60% | 60% | 60% | 100% | 80% |
| 1.1 | 1.1 | 1.1 | 1.1 | 1.1 | 1 | 0.8 |
| | %5 yellow add | %10 yellow add | %10blue decrease | 5% blue decrease | | |
| | | | | 3 % yellow increase | | |

| 14 | 15 | 16 | 17 | 1 |
|-------------------|-------------------|------------------|-----------------|----------------|
| | | | | |
| | | | | |
| | | | | |
| 5.372 | 3.958 | 2.79 | 2.001 | 2.12 |
| 50% | 50% | 50% | 50% | 50% |
| 100% | 100% | 100% | 100% | 100% |
| 1.1 | 1.1 | 1 | 1.1 | 1.1 |
| %10 decrease blue | 10% Decrease blue | 8% decrease blue | 8% decrease red | 8%Decrease red |
| | 5% add red | 6% add red | 8% add red | 8% add red |

PASS With Caustic Soda: PASS with Soda Ash

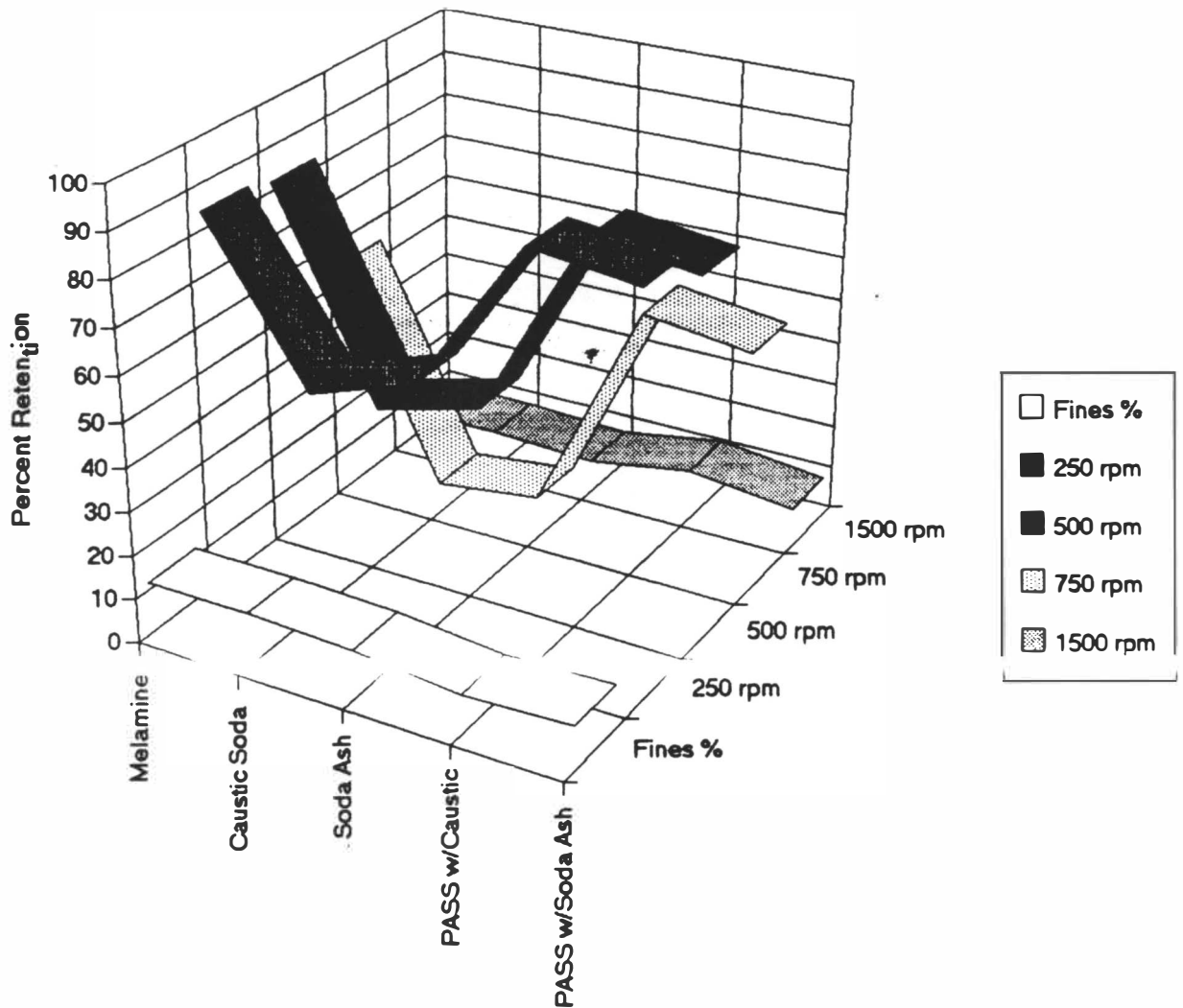


(4)

Britt Jar Retention Values

| | Melamine | Caustic Soda | Soda Ash | PASS w/Caustic | PASS w/Soda Ash |
|----------|----------|--------------|----------|----------------|-----------------|
| Fines % | 11.9 | 12 | 11 | 9 | 10 |
| 250 rpm | 84 | 50 | 58 | 92 | 89 |
| 500 rpm | 82 | 36 | 42 | 85 | 82 |
| 750 rpm | 54 | 7 | 10 | 59 | 56 |
| 1500 rpm | 9 | 9 | 8 | 12 | 9 |

Britt Jar Retention Values



(5)

Fade Values Compared to Standard

| | Melamine-DE | PASS/Caustic-DE | PASS/Soda Ash-DE |
|---------------------|-------------|-----------------|------------------|
| Lab value | 3.068 | 1.991 | 1.894 |
| | 3.214 | 1.921 | 2.125 |
| | 3.42 | 1.342 | 2.001 |
| Paper machine value | 3.302 | 1.729 | |
| | 3.219 | 1.811 | |

Fade Values Compared to Standard

