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A STUDY OF DUAL POLYMER RETENTION AIDS
FOR THE RETENTION OF TITANIUM DIOXIDE

USING THE DYNAMIC DRAINAGE JAR,
MINIDRINIER, AND HANDSHEETS

by

David E. Null

A Thesis submitted to the
Faculty of the Department of
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in partial fulfillment of the
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Western Michigan University

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ABSTRACT

Two types of dual polymer retention aid systems, a low molecular weight, high charge density, cationic polyamine with a high molecular weight, low charge density, cationic polyacrylamide, and the same polyamine with a high molecular weight, highly charged anionic polyacrylamide, were studied using the Dynamic Drainage Jar, the Minidrinier, and handsheets. Both systems gave higher retention than could be achieved using any of the retention aids alone, however, formation was a problem. Contact time and shear were shown to be important variables. All three testing methods were useful, the Dynamic Drainage Jar having an advantage due to its flexibility.

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LITERATURE SURVEY

Importance of filler retention

The use of fillers is now very important to the paper-maker. The principle benefits obtained from fillers are increased opacity and brightness. Fillers also improve smoothness, finish, printability, softness, adsorption and increase weight (1). The importance of fillers can be seen by the fact that about four million tons of nonfibrous materials are added to paper stock to produce about fifty four million tons of paper and paperboard each year (2).

Many benefits can be realized by increased retention of fillers. Some of these benefits are as follows:

1. Less consumption of fines;
2. A cleaner system and thus, less downtime;
3. Better paper and thus, fewer complaints and rejects;
4. Less pollution;
5. Increased production;
6. More versatile paper.

In this age of stiff competition and high raw material costs, the efficiency of filler retention as well as other things can very well determine the profitability of a mill.

However, to make matters more difficult, maximum filler retention may not be the best papermaking procedure (3). There are several reasons for this. One reason is because

of drainage problems.

Another reason is inefficient utilization of the pigment. This occurs when the filler is poorly distributed along the fiber. The effect of this is lower opacity and brightness than if the filler had been evenly distributed.

A third problem with high retention is non uniform formation. The goal is to get fiber-to-fine action with no fiber-to-fiber action (4). Poorly distributed fibers result in localized basis weight variations which gives poor optical and physical properties (4). This is solved by a highly dispersed fiber system which results in large fine losses during sheet formation prior to mat formation (5, 6).

Thus, the goal is to get high retention, good formation, good drainage and efficient filler retention. This probably requires a compromise.

Mechanisms of filler retention

The complex subject of filler retention can generally be explained by three different mechanisms. These are the mechanical, physio-chemical, and bridging mechanisms (7).

The mechanical mechanism is based on the process of filtration and entrapment. Filtration is the process of removing particles larger than the pore openings during sheet formation while entrapment is the physical collection of particles in the fiber lumens or in the fibril structure on the fiber surface (8). Thus, the size of the particles is important in this mechanism.

This type of of retention will predominate in a simple system of only fiber and filler. Mechanical retention may vary considerably with basis weight, machine speed, and other physical factors (9). "Two-sidedness" and low retention are common characteristics of this type of retention.

The physio-chemical mechanism is based on charge attraction. When cellulose is slurried in water, it develops a negative charge. Pigments such as clay and titanium dioxide develop similar negative charges when dispersed in water. When these dispersions are mixed, the like negative charges repel each other. Then, according to this mechanism, retention will be low (10).

However, if the electrokinetic charges could be manipulated to be equal and opposite, attraction could develop which would give high retention. This manipulation can be done by the use of a cationic retention aid. The cationic retention aids reduce the surface charges and allow cofloculation. This has led some observers to conclude that flocculation and fines retention are solely or predominantly determined by electrokinetic factors (11, 12).

Fraik offered the above two mechanisms for the theory of filler retention (13). However, these mechanisms do not explain why particles are not redispersed by hydromechanical action in systems of high retention. Also, they do not explain why anionic retention aids give adequate retention. These two situations can be explained by a mechanism

called bridging (7, 14).

Bridging is the mechanism where long polymer molecules are adsorbed on a particle leaving a large portion of the polymer free to be adsorbed on another particle. Thus, an actual molecular linkage is formed between the particles (15). Utilization of this mechanism requires that the particles come close enough together to allow the linkage to form. This can be accomplished by control of the electrokinetic charges. The tenacity of the anchor then becomes the important factor for full utilization of this mechanism.

It should be noted that the above three mechanisms probably do not completely cover the theory of filler retention. Other minor mechanisms, which may be variations or combinations of the above, also play a minor role. The formation of patches covering only a small proportion of the total surface and giving tenacious flocculation regardless of the net surface charge is one example (16-18).

Finally, it is obvious that filler retention is a combination of the three main mechanisms. Also, as retention increases, mechanical retention plays a smaller role. At high retention levels, the physio-chemical mechanism brings the particles together and the bridging mechanism gives a shear resistant attachment.

"Hard" and "soft" flocs

Another factor of filler retention is the degree of tenacity of the fiber-to-fine floc under shear. This is

important since a large amount of shear is developed on a paper machine. The terms "hard" and "soft" flocculation are used to describe this tenacity.

A soft floc can be defined as any combination of fiber and fines showing an improvement in overall fines retention at relatively low turbulence. If exposed to high levels of turbulence and allowed to reflocculate, the system will return to the original retention level. At high levels of turbulence the retention is low (19).

The best example of soft flocs is produced by addition of salts such as NaCl and $AlCl_3$. Another example of a soft floc is produced by low molecular weight polyethyleneimine. These examples show improved retention (although relatively low) which is reduced only slightly after exposure to high turbulence.

Polyethyleneimine at higher molecular weights shows hard floc formation. A hard floc can be defined as any stock system plus additive that exhibits good fines retention over a wide range of turbulence for brief periods but, will break down after subsequent exposure to high levels of turbulence for longer times (19). Retention after prolonged exposure to turbulence thus shows a marked decrease. High molecular weight cationic polyacrylamide is another example of a polymer which forms hard flocs.

Hard and soft flocs can be related to the mechanisms

of filter retention. Soft flocs form because of electrokinetic attraction with little or no bridging. Hard flocs are held together by bridging. When exposed to turbulence, the bridges initially hold together the floc. After longer exposure to turbulence, the bridges break and the loose polymer loops are adsorbed near their other ends. Thus, the bridges cannot reform. The significantly lower level of retention is now similar to that of a soft floc and is due to electrokinetic attraction. The reason soft flocs are not affected by turbulence is that turbulence does not affect the electrokinetic attraction.

Hard and soft flocs are important to the papermaker. Because of the turbulence on a paper machine, hard flocs must exist to get high levels of retention. Also, with too much turbulence, the hard flocs will break down and retention will be low.

Types of retention aids

There are two general types of retention aids-- salts and polymers. Salts are low molecular weight species such as aluminum sulfate, sodium aluminate, and sodium phosphoaluminate. They are the most widespread and among the oldest in use (1). Salts increase retention through the physio-chemical and mechanical mechanisms.

Polymers can be classified as naturally occurring, modified, or synthetic. Many naturally occurring gums, starches, and glues have been used for a long time as

retention aids. They themselves are poorly retained and thus add to a mill's BOD problem (1).

The chemically modified starches, such as the cationic starches, are more useful as retention aids than the natural starches. Also, they are completely retained and thus, add no waste problem (1).

The synthetic polyelectrolytes are far more effective and reliable than the naturally occurring or modified polymers. They can be classified as anionic, cationic, amphoteric, or nonionic. Most anionic retention aids are of the polyacrylamide type. Anionic polyacrylamides have an electrokinetic charge which is similar to cellulose and most pigments. Their use is highly dependent on pH and the aluminum salts present. Anionic retention aids form bridges between particles by anchoring to positive charges which were absorbed by the particles. Anionic polyelectrolytes tend to lose efficiency in alkaline solutions (1).

Cationic retention aids contain numerous cationic nitrogen-containing groups varying from free amines to quaternary ammonium salts. The electrokinetic charge on these polymers is opposite to that of cellulose fibers and most pigments. Therefore, flocculation can occur by the physio-chemical mechanism. Also, since the cationic retention aids have high molecular weights, bridging can occur when a polymer molecule becomes absorbed on adjacent

particles. Cationic polyelectrolytes tend to lose efficiency in acidic solutions (1).

Amphoteric retention aids were developed to be relatively independent of pH. They contain three basic units--two cationic quaternary ammonium units and carboxylated acrylamide anionic groupings. All are incorporated into the same polymer chain (1).

Nonionic polymers are primarily used as bridging agents. They are used in the presence of cationic materials.

Prediction and measurement of retention

One tool for the prediction of filler retention is the determination of electrokinetic potential or zeta potential. Theoretically, maximum retention will occur at a zeta potential of zero. Of course, the use of zeta potential requires the assumption that filler retention is largely dependent on the physio-chemical mechanism of filler retention.

The four methods used for the determination of zeta potential are electroosmosis, electroosmotic pressure, streaming potential and electrophoresis. These methods use the influence of a potential or pressure gradient on the system. By measuring the velocity of migrating particle or streaming liquid, or the pressure which develops, zeta potential can be calculated (20). Microelectrophoresis (a special case of electrophoresis) is the most

widely used technique for zeta potential determination and enjoys widespread acceptance (21).

Prediction of retention can also be made by trials on special instruments such as the Dynamic Drainage Jar and the Minidrinier. The Dynamic Drainage Jar is simply a container with a screen at its bottom. A 500 ml sample is placed in the container and a 100 ml aliquot is collected through the screen. A variable speed stirrer provides desired levels of turbulence. The fines loss can be found gravimetrically or turbidimetrically. A more detailed explanation is given by Unbehend (22). The advantage of this instrument is that it measures retention under turbulent conditions independent of most formation.

The Minidrinier Retention Tester is designed to measure retention under similar conditions. The Minidrinier Retention Tester is a wood-framed wire box with a removable slide and a drain-funnel to catch the white water. To perform a test, a sample is placed in the box and the slide removed. The filtrate is caught and the solids determined gravimetrically. A more detailed explanation is given by Werdouschegg (23).

A third way to predict retention is to make paper, either handsheets or with a pilot machine. Handsheets can be made on a Noble and Wood handsheet machine or a British Sheet Mold. Filler retention can be measured by ash tests and the effect of retention on opacity and

brightness can be measured. Handsheet studies can give indications of filler retention, but results cannot be expected to correlate well with commercial machines. One reason for this is that the high shear levels of a commercial machine are not developed during handsheet formation. Another reason is that retention with handsheets is not independent of the mat formation.

The ideal method for filler retention prediction is a pilot paper machine. The relative order of retention aid effectiveness can be extrapolated to a commercial operation with much more certainty. Again, the retention can be determined by ash values and the effects on opacity and brightness can be measured. Waddell suggests a procedure for planning, conducting, and evaluating a paper machine trial (24).

Studies of retention

The study of retention is very important to the papermaker. This is evidenced by the fact that so much work has been done with it. The written work is quite varied, ranging from the effects of agitation and retention aid molecular weight to the effects of carboxyl content of the cellulose and the pH of the system.

One area of more recent study is that of dual polymer systems. A dual polymer system can be defined as one in which two retention aids are used together, hopefully to attain higher retention than could be attained with either

retention aid alone. A dual polymer system is usually one in which a cationic polymer is added first, followed by an anionic polymer just before the stock reaches the wire. Theoretically, the cationic polymer reduces the electrokinetic charges and provides sites for the anionic polymer by adsorbing onto the fibers and fines. The anionic polymer then becomes anchored to the cationic sites forming bridges which lead to high retention (25).

Another possible dual polymer system is one in which a low molecular weight, high charge density, cationic polymer is added first, followed by a high molecular weight, low charge density, cationic polymer just before the wire. The theory here is that the low molecular weight polymer will reduce charge repulsion allowing the particles to come close together and also to prevent the higher molecular weight polymers from laying flat along a particle. The higher molecular weight polymer can then be adsorbed at vacant negatively charged sites on the particles and reach out for other particles forming bridges.

In one study using cationic and anionic polymers, Britt (2) has shown the following:

1. Dynamic retention of over 90%;
2. The importance of order of addition, cationic first, then anionic;
3. Similar effectiveness with clay, titanium dioxide, HiSil, and talc;

4. The effect of increased agitation;
5. That alum does not replace the cationic polyelectrolyte;
6. That cationic starch can be used in place of the cationic polyelectrolyte.

Moore has also done a quite extensive study with an anionic-cationic polymer system (26). He found the effects of alum, different cationic charge densities, and different anionic hydrolysis levels. Moore also suggested that proper selection of polymers may result in other benefits such as increased dry strength, wet strength, drainage, etc.

A final study which should be mentioned was a thesis done by Helminski (7). He showed that the best retention occurred near the isoelectric point. However, his results showed no advantage to a dual polymer (cationic - anionic) system.

OBJECTIVE

There are two main objectives for this thesis. The first is to evaluate a dual polymer retention aid system containing a low molecular weight, high charge density, cationic polymer and a high molecular weight, low charge density, cationic polymer. A dual polymer retention aid system containing a low molecular weight, high charge density, cationic polymer and a high molecular weight, high charge density, anionic polymer will also be evaluated for comparison. The evaluation will be done using the Dynamic Drainage Jar, Minidrinier, and Noble and Wood handsheets.

The second objective will be to compare the above mentioned tests.

EXPERIMENTAL DESIGN

Furnish

The furnish used was a fifty-fifty blend of Canadian softwood kraft and Canadian hardwood kraft. The pulp was soaked overnight and then refined in a Valley beater to 450 CSF. Distilled water was used throughout the experimental work.

The refined pulp was next centrifuged by placing it in a muslin bag in the centrifuge. After centrifuging, the pulp was allowed to dry by laying it out flat. The pulp was dried to insure that the pulp would not become a variable in the experimental work due to aging. Preservatives were not used since they would also become variables.

As furnish was needed, pulp and titanium dioxide were added to distilled water to give 0.5 % consistency. This furnish was allowed to stand overnight and then mixed at least one hour before using. The furnish was used within one week, storing in a cool place between use.

Titanium dioxide

The titanium dioxide used was TI-PURE[®] LWS, a water slurry of anatase. The slurry was diluted and aliquots measured as needed. The addition level was 10 % (based on the weight of B.D. fibers and pigment). Titanium dioxide was not added at the beater since much of it would be lost during centrifuging and unequal distribution of the

particles in the pulp could occur due to the high specific gravity of titanium dioxide. The slurry form was chosen since it is commonly used in industry and for its ease of use.

Retention aids

The retention aids used were supplied by American Cyanamid. Those used were Accurac[®] 41, Accurac[®] 135, and Accurac[®] 130.

Accurac 41 is a relatively low molecular weight, high charge density, cationic polyamine. This liquid sells for about 52¢ per pound. It is efficient over a wide pH range and its dosage will generally fall within 1.0 to 5.0 pounds per ton.

Accurac 135 is a relatively high molecular weight, low charge density, cationic polyacrylamide. This emulsion sells for about 53.5¢ per pound. It is diluted by adding to water and is then added to the furnish as close to the machine wire as possible. It can be used with or without alum and the addition level will generally fall between 0.5 and 3.0 pounds per ton.

Accurac 130 is a very high molecular weight, highly charged anionic polyacrylamide. This emulsion sells for about 54¢ per pound. It is diluted by adding to water and is then added to the furnish as close to the machine wire as possible. It is effective in stock systems containing alum and/or other cationic additives. The addition level will generally fall within 0.5 to 3.0 pounds per ton.

Addition levels

Accurac 41 was used at addition levels of 0.0, 2.1, and 4.2 pounds per ton. Accurac 135 and Accurac 130 were used at addition levels of 0.0, 1.8, and 3.6 pounds per ton. Then, since Accurac 41 was used together with either Accurac 135 or Accurac 130, a total of nine different combinations were tested.

Fines determination

Fines in this thesis include both cellulosic fines and inorganic particles. The fines were determined following the procedure in the "Information Manual" for the Dynamic Drainage Jar (27). This procedure is to place a 500 ml sample of 0.1 % consistency furnish in the jar which contains a 76 micron hole, 14.5 % open area screen, turn the agitator to 1500 RPM and then to 750 RPM, and then drain. The stock is then washed several times with wash water containing 0.01 % Na_2CO_3 and 0.01 % TAMOL 850. After 2000 ml of filtrate has been caught, 500 ml of water is allowed to drain through the jar and observed for clarity. Then the dry weight of the fiber on the screen is determined. From this and the exact consistency, the fines fraction can be determined.

Dynamic Drainage Jar tests

The Dynamic Drainage Jar was modified in that it had baffles on the side (about one-half inch wide) and an air supply attached to the bottom. The baffles were added to prevent swirling. The air supply helped prevent stock from

flowing through the screen before drainage. The screen used had 76 micron holes and 14.5 % open area. The general procedure for the use of the Dynamic Drainage Jar is listed elsewhere (27).

Two procedures were used for running a retention test. In the first, 500 ml of 0.5 % consistency stock was placed in the jar. Then, Accurac 41 was added and the agitator turned on. After 15 to 20 seconds, the high molecular weight retention aid was added. After 15 to 20 seconds more mixing, 100 ml was drained from the jar. The fines content was then determined in the liquid drained by filtering through pre-weighed filter paper, drying, and then reweighing. The % retention was determined by dividing the fines retained by fines present and multiplying by 100.

In the second procedure, everything was done the same except that drainage was started 3 seconds after addition of the high molecular weight retention aid.

Agitator speeds of 500 and 1000 RPM were used. For most addition levels, three tests were run at each speed.

Minidrinier testing procedure

The general procedure for use of the Minidrinier Retention Tester is given in the "Technical Information Bulletin" (28). The procedure used in this thesis was to measure 1000 ml of 0.5 % consistency stock in a 1000 ml graduate. Then Accurac 41 was added, the mouth of the graduate sealed with the palm of the hand, and inverted four times. Then, the high molecular

weight retention aid was added and the graduate again inverted four times. With the slide pressed firmly into the wooden frame, the stock was poured into the Minidrinier. When the stock motion stopped, the slide was removed with a steady, even motion.

The white water was caught in a beaker, and by filtering an aliquot of this through tared filtered paper, drying and then reweighing, the fines lost was determined. From this, the % fines, and the consistency, the % retention was determined.

The amount of the wire covered was also measured and recorded. This gives an indication of the drainage rate of the stock system.

Handsheets formation and testing

The final phase of this thesis was to make handsheets. The handsheets were made on the Noble and Wood handsheet machine using distilled water. Accurac 41 was added to the diluted stock in the handsheet mold and the perforated stirrer was moved up and down five times. Then, the high molecular weight retention aid was added and the stock again mixed by moving the stirrer up and down five times.

Formed handsheets were pressed using a blotter to prevent contamination from the felt. Drying was also done between two blotters to prevent contamination and scorching.

Conditioned handsheets were tested for brightness, opacity, and ash following TAPPI standards (29, 30, 31).

Formation was determined by placing the sheets on a light table and rating the formation between 1 (best) and 5 (worst). This was done without knowledge of the retention aids used for the sheets. Basis weight was also determined in grams per square meter. Finally, the scattering coefficients for the sheet and titanium dioxide were determined from the Kubelka-Munk theory.

TABLE I

Dynamic Drainage Jar (jar No. 1) results at 500 RPM using Accurac 41 and Accurac 135. Procedure: Accurac 41 added, mixed 15-20 seconds, Accurac 135 added, mixed 15 - 20 seconds, and then drained.

		ACCURAC 135		
		0 lbs/ton	1.8 lbs/ton	3.6 lbs/ton
ACCURAC 41	0 lbs/ton	29 ± 3	51 ± 6	67 ± 4
	2.1 lbs/ton	52 ± 3	61 ± 4	60 ± 1
	4.2 lbs/ton	47 ± 1	56 ± 4	58 ± 3

TABLE II

Dynamic Drainage Jar (jar No. 1) results at 1000 RPM using Accurac 41 and Accurac 135. Procedure: Accurac 41 added, mixed 15 - 20 seconds, Accurac 135 added, mixed 15 - 20 seconds, and then drained.

		ACCURAC 135			
		0 lbs/ton	1.2 lbs/ton	2.4 lbs/ton	3.6 lbs/ton
ACCURAC 41	0 lbs/ton	30 ± 2	40 ± 5	39 ± 3	37 ± 2
	1.4 lbs/ton	40 ± 3	41 ± 5	38 ± 2	40 ± 5
	2.8 lbs/ton	37 ± 2	40 ± 2	37 ± 1	
	4.2 lbs/ton	33 ± 5	34		

TABLE III

Dynamic Drainage Jar (jar No. 2, except for first column) results at 500 RPM using Accurac 41 and Accurac 135. Procedure: Accurac 41 added, mixed 15 - 20 seconds, Accurac 135 added, mixed 3 seconds, and then drained.

		ACCURAC 135		
		0 lbs/ton	1.8 lbs/ton	3.6 lbs/ton
ACCURAC 41	0 lbs/ton	29 ± 3	68 ± 2	79 ± 2
	2.1 lbs/ton	52 ± 3	90 ± 2	95 ± 1
	4.2 lbs/ton	47 ± 1	70 ± 9	79 ± 2

TABLE IV

Dynamic Drainage Jar (jar No. 2, except for first column) results at 1000 RPM using Accurac 41 and Accurac 135. Procedure: Accurac 41 added, mixed 15 - 20 seconds, Accurac 135 added, mixed 3 seconds, and then drained.

		ACCURAC 135		
		0 lbs/ton	1.8 lbs/ton	3.6 lbs/ton
ACCURAC 41	0 lbs/ton	30 ± 2	51 ± 5	66 ± 5
	2.1 lbs/ton	35 ± 1	58 ± 3	60 ± 2
	4.2 lbs/ton	33 ± 5	46 ± 3	49 ± 3

TABLE V

Dynamic Drainage Jar (jar No. 1) results at 500 RPM using Accurac 41 and Accurac 130. Procedure: Accurac 41 added, mixed 15 - 20 seconds, Accurac 130 added, mixed 3 seconds, and then drained.

		ACCURAC 130		
		0 lbs/ton	1.8 lbs/ton	3.6 lbs/ton
ACCURAC 41	0 lbs/ton	29 ± 3	54 ± 5	59 ± 3
	2.1 lbs/ton	52 ± 3	93 ± 1	97 ± 1
	4.2 lbs/ton	47 ± 1	80 ± 1	91 ± 2

TABLE VI

Dynamic Drainage Jar (jar No. 1) results at 1000 RPM using Accurac 41 and Accurac 130. Procedure: Accurac 41 added, mixed 15 - 20 seconds, Accurac 130 added, mixed 3 seconds, and then drained.

		ACCURAC 130		
		0 lbs/ton	1.8 lbs/ton	3.6 lbs/ton
ACCURAC 41	0 lbs/ton	30 ± 2	37 ± 1	48 ± 4
	2.1 lbs/ton	35 ± 1	67 ± 6	80 ± 3
	4.2 lbs/ton	33 ± 5	59 ± 1	74 ± 6

TABLE VII

Minidrinier results using Accurac 41 and Accurac 135. The top number is the % of fines retained, while the lower is the fraction of the wire covered.

ACCURAC 135

	0 lbs/ton	1.8 lbs/ton	3.6 lbs/ton	
ACCURAC 41	0 lbs/ton	60 3/4	68 2/3	79 7/12
	2.1 lbs/ton	77 7/12	92 2/3	93 2/3
	4.2 lbs/ton	69 3/4	96 3/4	85 11/12

TABLE VIII

Minidrinier results using Accurac 41 and Accurac 130. The top number is the % of fines retained, while the lower is the fraction of the wire covered.

ACCURAC 130

	0 lbs/ton	1.8 lbs/ton	3.6 lbs/ton	
ACCURAC 41	0 lbs/ton	60 3/4	61 All	64 All + (backwash)
	2.1 lbs/ton	77 7/12	91 5/12	95 1/2
	4.2 lbs/ton	69 3/4	89 1/2	89 5/12

TABLE IX

Noble and Wood handsheet results using Accurac 41 and Accurac 135.

ACCURAC 135

		0 lbs/ton	1.8 lbs/ton	3.6 lbs/ton
	0 lbs/ton	81.5 ± 1.1 81.5 ± 0.1 1 62.1 0.24% 0.0407	85.6 ± 0.8 80.8 ± 0.2 2 68.0 1.56% 0.0464 0.381	86.4 ± 1.1 81.1 ± 0.1 4 64.6 1.83% 0.0486 0.451
	ACCURAC 41 2.1 lbs/ton	90.7 ± 0.4 82.8 ± 0.2 1 67.5 4.10% 0.0610 0.526	91.1 ± 1.2 82.0 ± 0.3 4 70.3 5.38% 0.0590 0.374	91.0 ± 0.6 81.6 ± 0.2 4 72.3 5.12% 0.0551 0.315
		4.2 lbs/ton	89.8 ± 0.7 82.4 ± 0.1 1 66.3 3.79% 0.0584 0.498	89.9 ± 1.0 81.0 ± 0.2 4 69.0 4.39% 0.0547 0.351

KEY

Opacity
 Brightness
 Formation
 Basis Wt., g/m²
 % TiO₂ in Sheet
 Scattering Coefficient (sheet)
 Scattering Coefficient (TiO₂)

TABLE X

Noble and Wood handsheet results using Accurac 41 and Accurac 130.

		ACCURAC 130		
		0 lbs/ton	1.8 lbs/ton	3.6 lbs/ton
	0 lbs/ton	81.1 ± 1.1	85.2 ± 0.8	85.3 ± 0.8
		81.5 ± 0.1	81.2 ± 0.3	80.6 ± 0.2
		1	2	2
		62.1	64.5	62.4
		0.24%	1.25%	1.44%
		0.0407	0.0460	0.0473
		—	0.433	0.472
ACCURAC 41	2.1 lbs/ton	90.7 ± 0.4	91.5 ± 1.6	89.6 ± 1.4
		82.8 ± 0.2	81.2 ± 0.1	81.1 ± 0.3
		1	5	5
		67.5	68.4	68.7
		4.10%	5.68%	5.97%
		0.0610	0.0610	0.0541
		0.526	0.391	0.255
	4.2 lbs/ton	89.8 ± 0.7	89.7 ± 1.1	90.7 ± 1.1
		82.4 ± 0.1	81.1 ± 0.2	80.5 ± 0.2
		1	4	5
		66.3	66.8	63.7
		3.79%	4.70%	4.88%
		0.0584	0.0559	0.0599
		0.498	0.356	0.426

PULP

82.3 0.6
 80.4 0.2
 1
 62.6
 —
 0.0411
 —

DISCUSSION

In Table I, it can be seen that 4.2 pounds per ton of Accurac 41 is too high of an addition level. Accurac 41, being a relatively low molecular weight, highly charged cationic polymer works primarily through the mechanism of charge neutralization. Thus, 4.2 pounds per ton may have overshoot the isoelectric point giving an overall positive charge and repulsion of the particles. This is called polymer stabilization. This same trend occurs at all levels of addition of Accurac 135.

Also in Table I, it can be seen that Accurac 135 gives increased retention as the level of addition is increased. Since Accurac 135 has a relatively low charge density, the isoelectric point is apparently not overshoot. The Accurac 135 gives higher retention than Accurac 41 since it also uses bridging to retain particles. This bridging is resistant to shear. This system shows no advantage for the use of Accurac 41.

The data in Table II shows that when the system is agitated at a high shear for 15 to 20 seconds, retention is low. Neither retention aid was effective. Any bridges formed were broken and charge neutralization alone cannot achieve much retention at high shears.

Tables III and IV, when compared to Tables I and II, show the importance of the contact time between Accurac 135

and the stock. The contact time before drainage in Tables III and IV was only 3 seconds while that in Tables I and II is 15 to 20 seconds. The much higher retention in the second set of tables supports the theory that Accurac 135 achieves retention through bridging. Accurac 41 is assumed to give retention only through charge neutralization, its effectiveness being independent of contact time, and thus, it was not retested.

In Table III, the same trends are present as in Table I. In this table, however, Accurac 41 does improve the efficiency of Accurac 135. The retention at 2.1 pounds per ton of Accurac 41 and 1.8 and 3.6 pounds per ton of Accurac 135 is quite high. This can be explained as follows: Accurac 41 neutralizes the charges allowing particles to come together, but also still leaving negatively charged sites where the positively charged Accurac 135 molecules can attach and form bridges. Accurac 41 also helps keep the Accurac 135 molecules from laying flat along the first particle it attaches to and thus more bridges between particles can occur.

Table IV again shows the effect of higher levels of shear. The data also shows that bridges formed by the Accurac 135 polymers when Accurac 41 is present are not as tenacious as those formed when Accurac 41 is not present. The higher shear level breaks the bridges reducing retention.

Table V shows that using a combination of Accurac 41

and Accurac 130 can give very high retention. This high retention is explained as follows: Accurac 41, added first, reduces repulsion forces between particles and provides sites for Accurac 130 molecules. Then, when Accurac 130 is added, it attaches to the Accurac 41 molecules on adjacent particles forming bridges. Thus, shear resistant bridges are formed.

Table VI shows identical trends as Table V, except at the lower retention levels associated with the higher shear. Table VI, when compared to Table IV, shows that the Accurac 41 - Accurac 130 system gives flocculation more resistant to shear than the Accurac 41 - Accurac 135 system.

It appears that 2.1 pounds per ton of Accurac 41 used in the Accurac 41 - Accurac 130 system is a good level of addition. The use of Accurac 41 and Accurac 135 together, however, may be more effective at a lower addition level (maybe 1.0 to 1.5 pounds per ton) of Accurac 41. This is because Accurac 135, being positively charged, needs negative sites for attachment. Also, since Accurac 135 contributes positive charges to the system, the system may attain a positive zeta potential.

Two Dynamic Drainage Jars were used during this thesis. The first was on loan and had to be returned. The second had slightly smaller baffles and thus could have given higher retention results. Some combinations were run on both jars, and the second jar did give slightly higher retention results.

These were, however, within the variability of the test and without more tests, the jars cannot be concluded to be different. The fact that two jars were used can be overlooked.

As mentioned, the Dynamic Drainage Jars used had baffles. This differs from many jars used in other studies. The baffles were added to prevent swirling and were quite effective. They probably also reduce retention due to increased turbulence.

The Dynamic Drainage Jar appears to a good way to measure retention (a study with a papermachine would be needed to confirm this). The test gives good reproducibility and is easy to run. The test also has a lot of flexibility which is definitely an advantage. The test, however, does not give an indication of formation, drainage, or the final properties of the paper.

Tests were next run on the Minidrinier to test for formation and confirm the retention results of the Dynamic Drainage Jar. Formation was hard, though, to determine on the Minidrinier. There were differences, but they were not large enough to have much meaning. It was suggested that lower consistencies might give larger differences. Also, more experience and photographs could enable one to use the Minidrinier to predict formation.

The Minidrinier did prove useful as a measure of drainage. This is also very important to the papermaker.

Drainage is related to the fraction of the wire covered when a test is made. This, in turn, could be easily measured and there were significant results.

The overall retention is much higher on the Minidrinier than with the Dynamic Drainage Jar. This is because fines are retained on the Minidrinier by the mechanical mechanism as well as bridging and charge neutralization. Thus, this test may more closely correlate with papermachines. However, when studying retention, one would rather only measure colloidal forces since the papermaker does not change basis weight, machine speed, etc. when he needs higher filler retention.

Tables VII and VIII show the same general trends as the previous tables. Again, there is a synergistic effect when using both Accurac 41 and Accurac 135 and also, Accurac 41 and Accurac 135. The retention using The Accurac 41 - Accurac 135 system was as good as that using the Accurac 41 - Accurac 130 system. This is explained by the fact that there is no shear present before the slide is removed and thus electrokinetics plays a larger role and the tenacity of the floc plays a smaller role.

The drainage results using the Minidrinier were interesting. When Accurac 130 was used alone, drainage was very poor. This is because adding negative charges to the system tends to disperse the particles. When Accurac 41 and Accurac 130 were used together, the drainage was very good.

This is because tight flocs are formed. The drainage in Table VII was good, but slower. The fast drainage in Table VIII may have also reduced retention slightly.

The Minidrinier is a good test, but it lacks the flexibility of the Dynamic Drainage Jar. It is also more cumbersome to run and more subject to errors. Also, due to slow filtering, aliquots had to be taken of the filtrate to determine the fines content.

Improvements could be made to the Minidrinier. Two suggested improvements are a better design (tighter fitting and easier washing and handling) and the addition of some sort of agitator.

The handsheets were made to test for the formation which could not be tested before. Table IX again shows that retention decreases when too much Accurac 41 is added. The formation was quite good using only Accurac 41. This is because no tight flocs are formed using Accurac 41. Retention was good compared to other combinations since there was no turbulence present. The scattering coefficient for the sheet shows that the increased retention also improved sheet properties.

When Accurac 135 was used alone, the retention and scattering coefficient for the sheet were both low. Lack of turbulence may actually hinder bridging since there may not be enough contact between particles to allow bridges to form. The low consistency used for handsheets may also

have this effect. The flocs which did form, however, were enough to disrupt the formation.

The combinations of Accurac 130 and Accurac 41 gave the highest retention results. The formation of these sheets was poor and thus the scattering coefficient for the sheets was not as good as when 2.1 pounds per ton of Accurac 41 was used alone. The scattering coefficients for titanium dioxide were also relatively low, showing again that the titanium dioxide was used inefficiently.

The relatively low retention results in Tables IX and X can be explained by the low consistency. The low consistency limits flocculation and also creates a lot of suction as it drains.

Handsheets have shown how important formation is to sheet properties. The results may not correlate well with papermachines, but they do show that formation problems may occur with certain combinations of retention aids. As Britt writes, new headboxes with more turbulence may be needed to effectively utilize the higher retention attained with dual polymer systems.

CONCLUSIONS

Several conclusions can be made from this study.

These are as follows:

1. Mechanical, physio-chemical, and bridging are useful mechanisms to predict and explain the retention of titanium dioxide.

2. Low molecular weight retention aids are not real effective, especially at high turbulence levels.

3. The use of dual polymer systems can give higher retention than could be attained through the use of a single polymer.

4. Formation is a potential problem when dual polymer systems are used.

5. The dual cationic system gives better formation but less resistance to shear than the cationic - anionic system.

6. Increasing the contact between the high molecular weight retention aids and the stock before drainage reduces retention.

7. Increasing shear lowers retention.

8. The Dynamic Drainage Jar, Minidrinier, and handsheets are all useful ways of studying retention, each having advantages over the others.

9. The Dynamic Drainage Jar is probably the most useful because of its flexibility.

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