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The Effects of Polymer Molecular Weight on Colloidal Retention and the Bridging Mechanism

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THE EFFECTS OF POLYMER MOLECULAR WEIGHT ON COLLOIDAL
RETENTION AND THE BRIDGING MECHANISM

by

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A Thesis Submitted
to Dr. Raymond L. Janes
in Partial Fulfillment of
the Course Requirements for
The Bachelor of Science Degree

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ABSTRACT

A review of retention is presented. Included are discussions concerning retention mechanisms, variables which affect retention, variables affected by retention and various retention aids. A detailed experimental procedure involving the use of the dynamic retention/drainage jar is included along with several modifications of the apparatus.

The purpose of the experimental work was to study the effects of polymer molecular weight on retention and the bridging mechanism. Two cationic retention aids of low and high molecular weight along with two non-ionic "bridging agent" retention aids were employed. Various combinations of these chemicals were studied at different levels of addition and under different shear conditions. The results are discussed as they relate to maximum retention, maximum retention and level of addition, percent improvement at various levels of addition, shear and shear resistance.

It was found that in most cases higher molecular weight retention aids give higher retention than lower molecular weight retention aids. High molecular weight polymers are more efficient than low molecular weight polymers at high shear but less effective at low shear. The high molecular weight bridging agent is more effective than the low molecular weight bridging agent regardless of shear. Increasing molecular weight gives increased stability to retention reduction by shear. Bridging does occur and increases with increasing molecular weight, to a point. Molecular weight and charge are both important in bridge formation.

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INTRODUCTION

A thorough investigation of the effect of molecular weight on the bridging mechanism during retention necessitates a complete understanding of the entire area of retention. To isolate one certain phenomenon, which probably occurs in conjunction with several others in a microscopic environment, requires that the system must be controlled in such a way so as to produce the desired mechanism while rendering all other mechanisms either constant or non-existent. The purpose of this paper is to present a report as complete and informative as time and space will permit.

I. Retention Defined

Retention is one of the most important, one of the least understood, and, potentially, one of the most economically rewarding areas of concern for a modern papermaking mill.

As pointed out by Walkush and Williams (2), retention by the pulp fibers of cellulosic fines and other colloidal particles present in the furnish, such as rosin size, asphalt and latex emulsions, acid and direct dyes, starch, dry strength additives and filler pigments, is a very complex physichemical problem.

Purpose

Basically, retention can be defined as holding in the moving web the various additives which compose the final sheet of paper. Increased retention is needed to produce more paper of better quality

at lower operating costs while reducing losses of raw materials and increasing reuse of water within the mill. Improved retention can also lead to reduced BOD loads in the mill effluent and less chemical deposits in stock line, headbox, wire pit, seal pit and save-all surfaces which could eventually break away and cause wet end breaks and expensive downtime.

First Pass vs. Over-all Retention

Retention occurs in several ways, all of which will be discussed in greater detail later in this report. Before moving on to how retention is brought about or what affects or is affected by retention, a more concise definition of retention is needed.

Retention can be expressed and calculated in several ways. Lodzinski (36) points out that retention can be expressed as first pass or overall retention. These two categories can be further divided into first pass and overall retention of total suspended solids, ash and cellulosic fines.

First pass retention, also known as one pass, single pass or couch retention, is an expression of the amount of a substance, whether it be total suspended solids, ash or cellulosic fines, remaining in the final sheet compared to the amount of that same substance contained in the headbox. It is usually expressed as a percentage.

Overall retention is an expression of the amount of material remaining in the final sheet compared to the amount of material supplied before headbox dilution, i.e. in the stuff box.

As is evident, just stating a retention value is not sufficient. It must be specified whether or not the value quoted is first pass or

overall retention and if it deals with retention of total suspended solids, filler or cellulose fines.

Frankle and Sheridan (3) define first pass retention, R_t , equal to $\frac{H-T \cdot Y}{H}$ where H is the headbox consistency, T is the white water consistency, and $Y = .90$. They define Y as the fraction of total headbox stock volume which passes through the wire. In previous work, Y was taken to be unity, but this tends to be an underestimate of first pass retention. Rather, they assume $Y = .90$ because only 90% of the total headbox stock volume actually passes through the wire and into the white water. The remaining 10% stays with the sheet and passes on to the press section. The value for Y is by no means a constant value. It will differ from machine to machine depending on many different factors.

Frankle and Sheridan (3) developed an easy, effective method for determining first pass retention by relating retention to sewer losses. The assumption is made that such things as cleaners, screens and save-alls operate at about the same efficiency and that these losses are proportional to the load on the save-all. Therefore, if the losses increase, that would indicate a corresponding decrease in retention.

The separation of the three constituents, total suspended solids, ash and cellulose fines, can be accomplished by wet screening. The wet screening will separate the long fiber fraction from the fines, and subsequent ashing of the filtrate separates the ash from the cellulose fines. This method will be used in the experimental portion of this report.

Lodzinski (36) shows that the only samples required to complete a total retention study are those from the headbox, stuff box, white water tray and final sheet. These will provide all the information necessary to calculate retention values after ash tests have been run. For a more rigorous and thorough discussion of all aspects of retention calculations, consult Lodzinski (36).

II. Mechanism of Retention

Retention is brought about in the papermaking system by many complicated mechanisms. Several authors (2, 9, 17, 19, 25, 31, 35) have investigated these mechanisms. Naturally, they sometimes agree and sometimes disagree on which mechanisms are the most significant. Many factors affect which type of mechanism will prevail in which system. Often times it is a combination of two or three mechanisms which results. The basic types are as follows.

Mechanical Filtration

The fourdrinier wire is the forming surface for the sheet of paper. As the stock flows onto the wire, the long fiber portion of the furnish is trapped by the wire and held in place. Particles which are too small to be filtered out by the wire mesh pass through the wire and are lost from the sheet to the white water. This passage of fine and filler particles gradually decreases as the fiber mat continues to build up.

The addition of a chemical to the furnish may cause these small fines and filler particles to be flocculated or coagulated, thereby increasing their tendency to be trapped by the fiber mat. Whether flocculation or coagulation occurs depends on the type and amount of chemical added. There are flocculating retention aids and coagulating reten-

tion aids. LeMer and Healy (35) distinguish between the two types in this way. They define coagulation as the "driving together" of the particles to form a tightly knit group. Flocculation, on the other hand, is the process of forming a "loose fibrous structure". "It is a loose, three dimensional network having pores which permits easy filtration. A floc is generally much larger than a coagula."

The filtration takes place in the pores of the fiber mat and is purely a mechanical process. It should not be confused with fiber-filler agglomeration which will be discussed later in this paper.

Mechanical Attachment

Fraik (13) described mechanical attachment 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 mechanical theory of retention, which includes filtration and attachment, is probably better classified as media filtration as explained by Johnson (19). Particles are retained during media filtration by the internal structure of the filter media. This would include both the pores of the web and the fibrils of the fibers and fines.

Media filtration is affected by several papermaking parameters. Increasing sheet weight (basis weight) will obviously increase retention through the pore filtration mechanism. Increasing refining will increase retention by way of mechanical attachment. Reducing machine speed and lowering suction box vacuum, as well as installing finer wires, will serve to increase retention due to mechanical causes.

Physichemical -- Charge Attraction

Charge attraction occurs when two oppositely charged particles are brought together. They have a tendency to attract each other and form a floc which is more easily retained. Unfortunately, this does not occur too often in a papermaking system unless an agent is added which will chemically alter the prevalent electrical charge of the system. The fines, filler, and fiber portions usually all carry a negative (anionic) charge and tend to repel each other when the particles approach closely (22).

Physichemical -- Co-flocculation

Flocculation can occur in the absence of electrokinetic charges on the individual particles. Whether flocculation occurs or not depends on several things, such as shear and pH.

The necessary electrokinetic condition for flocculation is usually brought about by the addition of a chemical retention aid which serves to suppress the electrical double layer, thereby allowing the respective constituents to form a floc. Depending on the retention aid used, the colloidal forces formed may or may not be shear resistant.

Walkush and Williams (2) maintain that there are three factors which affect co-flocculation: the collision process encountered in the system, the aggregate formation, and the aggregate strength.

Strazdins (7) points out that the coincidence of maximum furnish freeness and furnish drainage, with the isoelectric point, verifies the significance of charge neutralization in flocculation.

LeMer and Healy (35) obtained maximum drainage of a calcium phosphate coagula corresponding to the point of maximum coagulation. This points out that, although flocculating and coagulating retention aids were used, maximum drainage and/or retention was still achieved.

Bridging

Bridging is the mechanism by which a long chain polymer forms a connection between two or more particles. The connection may be between cellulose fines and fillers, between two pigment particles, between fibers and pigment particles, or even between two fibers.

There are two types of bridging which have been proposed by LeMer and Healy (35). See Figure 1. First, bridging can occur when one end of a polymer chain contacts and is adsorbed upon one particle, while the other end of the same chain attaches to another particle. The second method involves bridging through loops and tails. In this mechanism, a long chain polymer adsorbs on the particle surface at various locations along the polymer chain length while the remaining, unattached portions of the polymer extend out into the solution ready to form bonds with other available particles.

One investigator (4) found that bridging gave flocs increased shear stability while another (24) has reached just the opposite conclusion. Of course, it depends upon the type and composition of the system. This is one area with which the experimental portion of this report will deal.

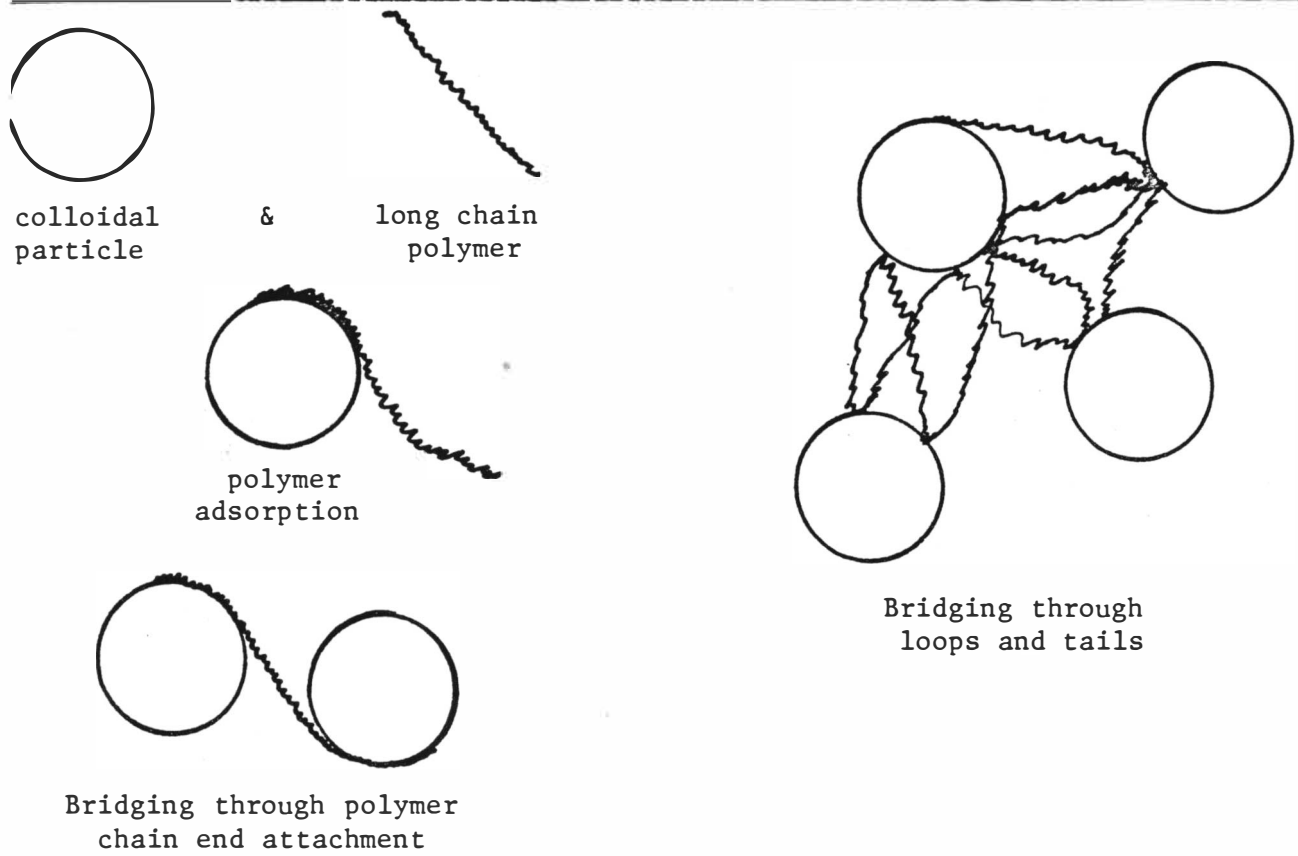
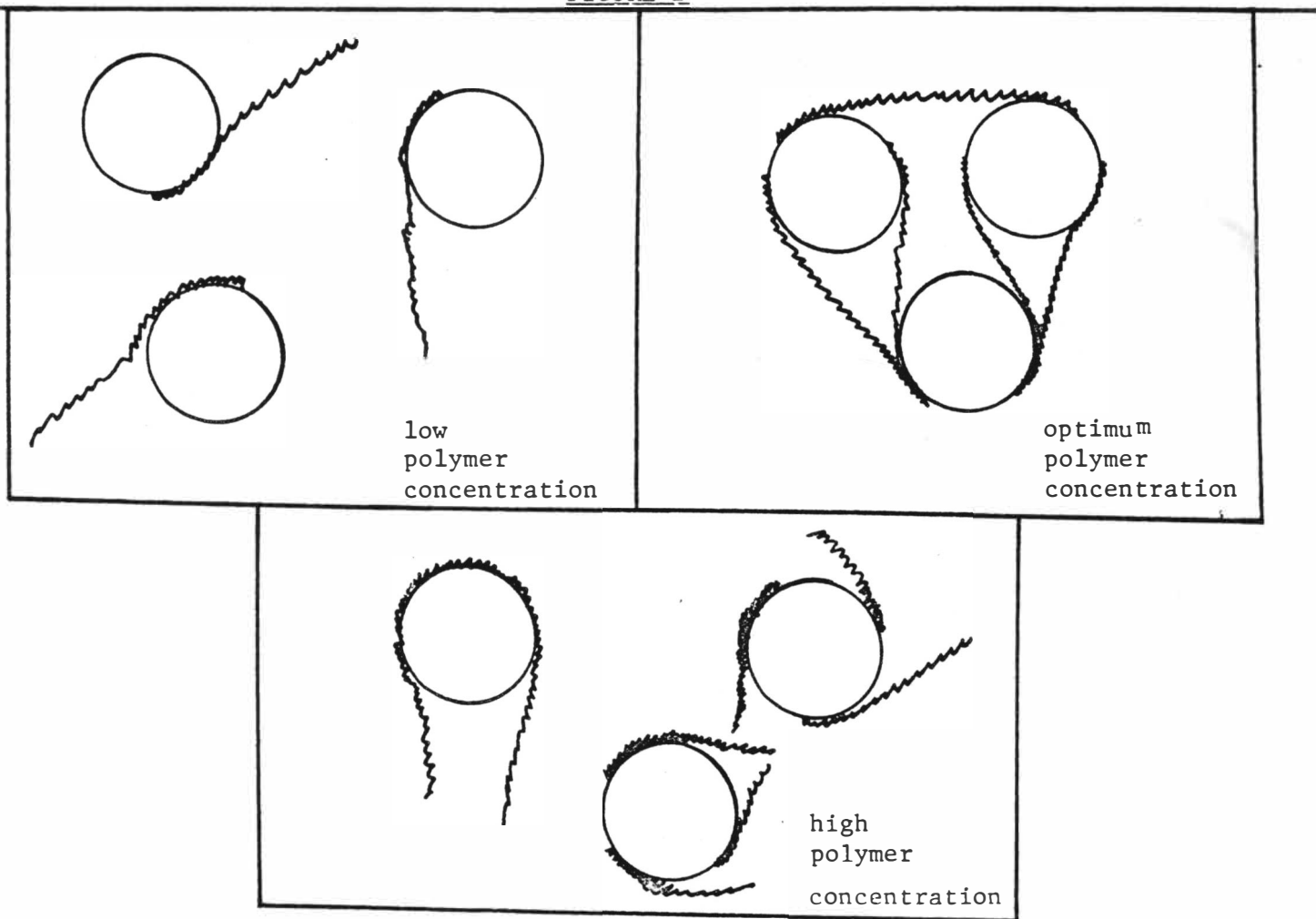


FIGURE 2



Bridging requires that the places of attachment be strong. Britt (31) suggested the preadsorption of a small, highly cationic molecule could provide just the right conditions for good bridging to occur. Bridging in this case would be accomplished with a long chain, anionic polymer. Theoretically, increased bridging would be a necessary result from increasing polymer molecular weight. LeMer and Healy (35) supported this conclusion. They found that, as polymer molecular weight was increased, flocculation tended to increase. They found, too, that the drainage/filtration rate reached a maximum at an optimum molecular weight in the range of 3 to 3.5 million for the calcium phosphate system they were studying. They suggest that this is the optimum molecular weight for optimum bridging to occur.

Contrary to LeMer and Healy's findings, Swanson (24) found that increasing the molecular weight of the bridging agent caused a slight increase in retention but did considerable harm to formation. He considered that the total charge contributed by the polymer was the most important factor in determining retention, and that molecular weight was of secondary importance.

LeMer and Healy (35) also discussed the importance of polymer concentration to bridging. Too little polymer will leave available bridging sites unoccupied. Too much polymer will cause coating of the particle surfaces and reduce the available bridging sites. They state that, "As the fraction of the surface covered increases, the chance of extended segments adsorbing and completing bridges decreases, ... as more and more polymer is adsorbed, each incoming polymer molecule

finds progressively less and less surface on which it can become attached." Just the right polymer concentration will provide the required number of adsorption sites, without leaving any sites unused by the polymer. Figure 2 is a graphic description of this polymer concentration theory as given by LeMer and Healy (35).

The bridging mechanism may form soft or hard flocs, depending on several things. There is not complete agreement on this topic either. Hard flocs are those which are briefly resistant to breakdown over a wide range of turbulence. Hard flocs do not reform, as soft flocs do, once the applied shear is removed. LeMer and Healy (35) point out that the degree of adsorption and flocculation depends on both the time duration and intensity of the applied shear.

Swanson (24) has found that the shear resistance of a floc formed by a charged polymer is independent of the polymer molecular weight. Unbehend (9) has found that, with increasing molecular weight, better shear stability results, but the flocs do not reform after the shear is removed. Contrary to this, Swanson (24) found that soft flocs formed by high molecular weight polymers tend to reform rapidly after excessive agitation is removed.

Undoubtedly, these contradictory and varied conclusions stem from the fact that each person was studying a different system and may have had other factors contributing to the end result. It is difficult, if not impossible, to extend conclusions from one study to predict what will occur in another, especially in the field of paper dynamics.

In summary, then, these are the requirements for bridging to occur as outlined by LeMer and Healy (35):

- a) that extended segments are available;
- b) that they are of sufficient length and number;
- c) that free surface for bridge sites is available.

Dispersion results if:

- a) The surface becomes so covered that there is insufficient free surface for bridging;
- b) the extended segments are so long as to be unable to overcome the thermal motion of individual particles in the floc;
- c) the extended segments physically interfere with one another to prevent bridge formation.

Considering these requirements and the contradictions described above, these are the questions that this study will attempt to answer: (1) Is retention dependent on polymer molecular weight, increasing as polymer molecular weight increases? (2) Is molecular weight or charge distribution/charge density the controlling factor in bridging? (3) Does bridging occur at all and, if so, what causes and influences it? (4) Are the flocs formed by bridging more resistant to shear with increasing molecular weight? (5) Do the flocs reform readily after high shear is removed?

Patch Model

The final mechanism of retention is referred to as the patch model, as discussed by Goossens and Luner (18). For patching to occur, partial neutralization of the particles is brought about by adsorption of a small, cationic polymer. The driving force for coagulation is then the Van der Waal forces of attraction between the negative and positive sites on the different particles. See Figure 3.

In a paper system it is easy to see how this may be accomplished. A small, highly charged cationic polymer could be preadsorbed onto the surface of fibers, fines and filler alike, leaving gaps of negative charge exposed. The cationic and anionic areas exhibit affinity for each other, causing coagulation.

As suggested by Britt (31), the preadsorption of a small, highly cationic molecule could provide just the right conditions for good bridging to occur. Therefore, coupling this patch model with long chain, anionic polymers may provide excellent results. Some work is now being done on this cationic-anionic system and seems to be giving excellent results.

It is quite obvious that none of the mechanisms act totally on its own in any papermaking system. Each one is interrelated to the others, and sometimes the line between them seems narrow and foggy. Once a basic knowledge of the mechanisms is obtained, attention must be turned to factors which tend to influence retention.

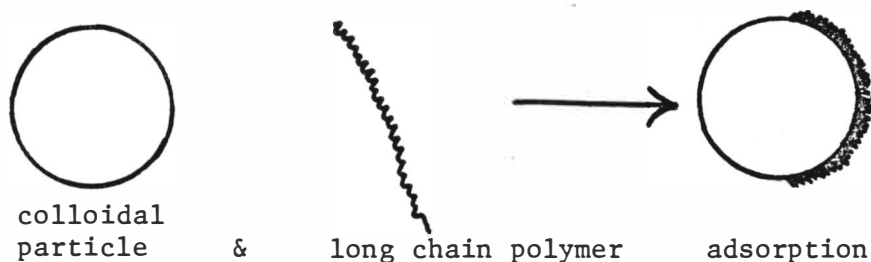


FIGURE 3

III. Parameters Which Influence Retention

There are many varied and interrelated factors which tend to influence retention during the papermaking process. Some of these occur

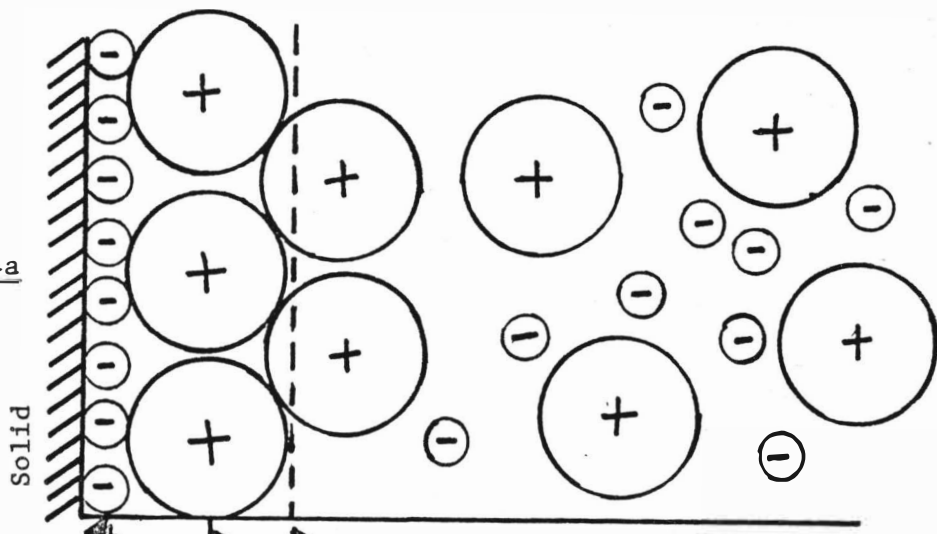
before the furnish even gets to the wire; some act while the stock is on the wire; and some are inherent in the type of materials with which you are working.

Strazdins (7, 20, 21, 22, 28) and others (1, 5, 6, 8, 11, 13, 18, 23, 30, 34) have pointed out several factors which influence retention. Changes in the surface area and accessibility of the cellulose to the retention aid are of prime concern. The carboxyl content of the cellulose, the presence of foreign ions (especially polyvalent cationics), polymer size, bonding ability, pH, contact time, shear, zeta potential, temperature, basis weight, freeness (refining and waste paper reuse), machine speed, machine mechanical action, water type, alum level, filler type, stock dilution, wire length and mesh size are all parameters which must be considered when dealing with retention. All of these are important. Some have been well investigated. Some need more work, and some are given constants with which the mill must work.

Zeta Potential

Zeta potential, or electrokinetic potential, is the potential developed between the fixed, adsorbed ions on a particle and the ions which remain in solution. This potential is shown graphically in Figure 4b. Both Figure 4a and 4b are reproduced from an article by Williams and Swanson (36) and are models of the electrical double layer as given by Stern and Graham. Figure 4a is a picture of the adsorbed ions and counter ions, with the remaining counter ions in solution. The potential developed at the interface between the Stern Region and the Gouey-Chapman Region is the zeta potential.

FIGURE 4a



Potential determining ion layer

Shear plane

Outer Helmholtz plane

Inner Helmholtz plane

Stern region

Gouy-Chapman region

Distance from surface

FIGURE 4b

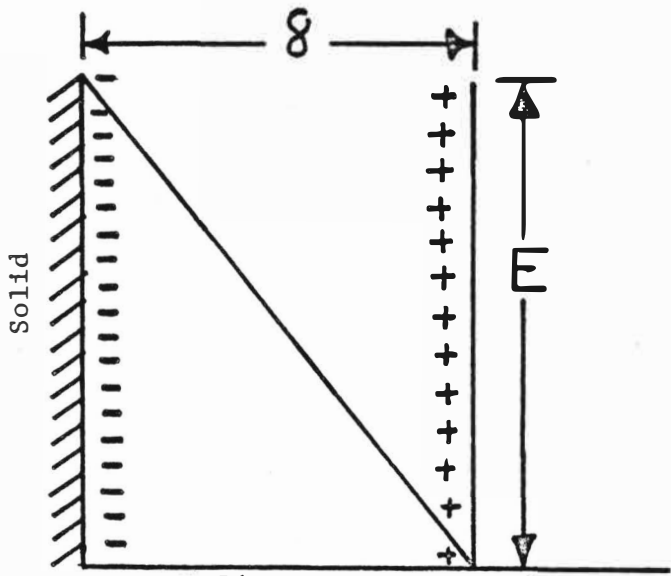
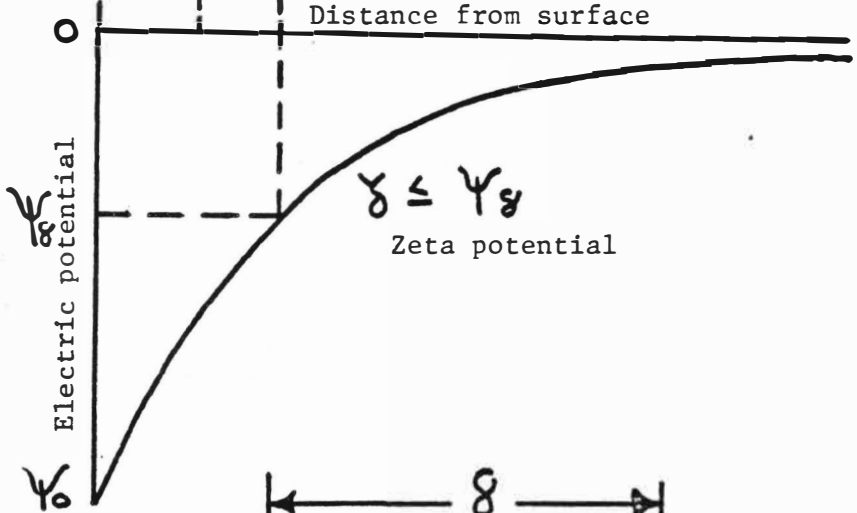


FIGURE 5

Walkush (2) pointed out that zeta potential is an indication of the state of the electrical double layer. As zeta potential decreases upon addition of a chemical agent, the electrical double layer becomes more suppressed. Eventually, when the zeta potential reaches zero, the electrical double layer is totally suppressed, and flocculation or coagulation usually occurs rapidly.

Strazdins (7) shows that, as the system's zeta potential moves toward the isoelectric point, or zero zeta potential, flocculation and drainage rates approach maximum values, and apparent density and formation approach minimum values.

Figure 5 was given by Williams and Swanson (36) as a description of the Helmholtz and Perrin model of the electrical double layer. The potential difference, ΔE , decreases as you move across the thickness, δ , of the double layer. The potential is given by the equation 1 where:

ϵ is the dielectric constant, and q is the surface charge density.

$$\Delta E = \frac{4\pi\delta q}{\epsilon} \quad (1)$$

Figure 4 is a more realistic picture of the electric double layer as it is thought to exist. This figure was explained above and shall not be dealt with here.

Williams and Swanson (36) state that "The net potential energy of interaction of colliding particles is the sum of the repulsion energy and attraction." Equation 2 as given by Williams and Swanson (36) describes this mathematically

$$V_{\text{net}} = V_R + V_A \quad (2)$$

Williams and Swanson (36) give the following function which defines the net potential energy of interaction, as described above, for two closely spaced parallel plates ($< 10\text{\AA}$) under weak interactions ($Xd \gg 1$) using symmetrical electrolytes.

$$V_{\text{net}} = \left(\frac{64\pi kT}{X} \right) \gamma^2 \exp. (-2 Xd) - \left(A/48d^2 \right) \quad (3)$$

n = concentration of the electrolyte in the dispersion medium

K = Boltzman's constant

T = absolute temperature

X = the reciprocal of Debye radius (Debye-Huckel theory)

d = distance between the flat plates

A = London-Van der Waals' constant, about 2×10^{-12} ergs

γ = $[(\exp. Z/2) - 1] / [(\exp. Z/2 + 1)]$

Z = $Z_1 e \psi_s / kT$

e = charge on the electron

Z_1 = valence of the counterion

ψ_s = electric potential at the onset of the diffuse double layer

Williams and Swanson (36) point out that Verwey and Overbeek have studied a system of collecting spheres. They state that this function closely approximates what happens in a system containing colliding spheres, one much like a papermaking system.

Zeta potential is usually measured by sampling the tray water and running the tests on these samples. Some investigators argue that this is not a valid method because, they contend, the fines carry a much

higher charge density than the long fiber fraction. Strazdin (20) settled the dispute when he proved that the zeta potential of the fines is the same as that of the long fiber fraction.

There are four main procedures for the determination of zeta potential as summarized by Sennet et al. (14). They are: Electrophoresis, Sedimentation potential, Streaming current or potential, and Electroosmosis. Table I is a reproduction of one presented by Sennet et al. (14). It summarizes the various methods and their characteristics.

TABLE I Procedures for Measuring Electroporetic Potential

Name of Procedure	Property Measured	Mobile Phase	Example
Electrophoresis	Particle mobility	Particles	Microelectrophoresis Moving boundary Mass transfer
Sedimentation potential	Voltage	Particles	Sedimentation potential
Streaming current or potential	Current or voltage	Liquid	Streaming current or potential
Electroosmosis	Pressure Velocity	None Liquid	Electroosmosis

Meersman (37) gives these basic descriptions of the four procedures:

Electrophoresis - particle movement is caused when the particles, which are suspended in a liquid, are subjected to an electrical potential difference. This movement is toward the poles carrying a charge opposite to that of the particles.

Sedimentation potential - a potential difference develops when charged particles are allowed to settle from a dispersion.

Streaming current - a current develops when a liquid is caused to move past a charged surface such as the wall of a glass capillary tube.

Electroosmosis - an applied electrical potential difference causes movement of a liquid through a capillary tube.

Of the electrophoresis type of determination, three separate methods have evolved. Microelectrophoresis has developed into the most widely used method for the determination of zeta potential. In this process the motion of small, nonsettling particles in an electric field is observed and measured under a microscope.

A relatively new technique for surface charge measurement has been developed by Halabisky (33). It is a titration method that involves measuring the amount of anionic and cationic polymer which adsorbs on the fines, fillers and fiber in the furnish. The ratio of the amount of each polymer adsorbed is an indication of the sign and magnitude of surface charge.

Temperature

There is a noticeable lack of literature on the effect of temperature on retention. Some thesis work has been done (38) and the conclusion is that increases in temperature increase retention. Increasing temperature tends to decrease surface hydration and increase particle free energy, thereby making flocculation more probable (36).

Basis weight

It is an obvious result that when basis weight increases, retention will increase due to increased filtration. Another consideration, as pointed out by Frankie and Sheridan (3), is that retention

increases as basis weight increases, not so much because of increased filtration, but because of the decrease in fines content in the head-box.

Refining

As the stock is refined more and more, the hydrodynamic surface area of the fiber (the surface area of the exterior) increases. The fines fraction also increases. The additional exposed fibrils tend to increase retention through mechanical entrapment. The fines will preferentially adsorb filler and additive particles, especially clay, as pointed out by Williams (29).

Refining obviously decreases stock freeness, but not so obvious is the fact that increasing refining causes increases in the cationic demand (the amount of cationic polymer needed to bring the fibers to the isoelectric point). The increased surface area is one reason the cationic demand increases, because it increases the number of carboxyl groups exposed (the carboxyl groups determine the charge on the fiber system). The increased refining also opens up the more inaccessible regions inside the fiber, thereby increasing the cationic demand.

Machine Mechanical Action

This is one area of retention control which is relatively fixed unless it is the purpose to specifically improve retention in the machine related area. This does not mean, however, that this area is insignificant as far as retention is concerned.

In the past, the mechanical action of the machine drainage elements had a tremendous effect on retention. With the development of foils and other related equipment, the mechanical action has become much gentler.

Urick and Fisher (11) summarized six causes of drainage which are also the six machine related areas which can effect retention: first is the hydrostatic pressure from the weight of the stock on the wire; second, the pressure from the angular impingement of the stock on the wire; third, the vacuum forces due to motion of the wire over the table rolls and/or foils; fourth, the externally generated vacuum forces such as vacuum boxes and the suction couch; fifth, pressure from rolls, such as a dandy roll; and sixth, pressure in wet and suction presses.

Shear

Shear is the major factor encountered on the papermachine which causes loss of retention. If there were no shear forces many problems encountered in attempts to obtain increases in retention would be avoided. As shear increases, retention decreases. The flocculated fines and fillers are removed or deflocculated from each other or from the fibers. In the case of hard flocs, this will reduce retention upon shear reduction since the flocs do not reform. In the case of soft flocs, they will reform once the shear is removed if there is sufficient time before sheet formation. As discussed before, shear causes the fibers to become increasingly electronegative, thereby increasing the cationic demand.

Point of Addition

Generally, retention aids are added at the point of thick stock dilution. This is done so as to flocculate the newly added filler and fines along with those which are brought in with the recirculated white water.

Swanson et al. (1) found that increasing the recovery time after the polymer is added will allow for recovery of most of the lost flocculation. If the polymer is added too soon, it will not get mixed in well enough to produce even flocculation. If it is added too far back, and if it is a hard floc-forming polymer, it may not be able to withstand the additional shear encountered in the system.

pH

Most papermaking systems have pH values in the range of 4-6 due to the presence of various electrolytes. The isoelectric point for most pulps occurs in this same range. The higher the pH, the more electronegative the fiber becomes (16).

Fraik (13) reported that retention is a function of the pH encountered when the pigment was added. His study showed that the retention of TiO_2 reached its maximum at pH 5-6 (13, 23).

Water Type

The presence of water hardness, CaCO_3 , can aid in the retention of fines and fillers. It has been found that the Ca^{++} ions react with the OH^- carboxyl groups to partially neutralize the electro-negative charge inherent in the system. It does this by specific adsorption of the Ca^{++} ions onto the fiber surface (36).

Carboxyl Content

Britt (31) has found that zeta potential is closely related to the carboxyl content of the pulp, increasing as the content increases and decreasing as the content decreases. Pulps with a high carboxyl group content will absorb large amounts of cationic polymer before undergoing neutralization, and then, charge reversal.

Strazdin (7) states that it was originally thought that retention was due to ion exchange. He then goes on to prove that ion exchange is a result, not the cause of, polymer adsorption on the fiber.

Filler Type

In his study, Williams (29) points out some very interesting results on a study performed on TiO_2 and clay fillers. When TiO_2 is to be retained, the presence of fines is not essential, as the TiO_2 particles will be retained upon the fibrils of the individual fibers. The TiO_2 particles in the white water are attached to the pulp fines or to each other. The forces of attraction between these particles are apparently weak (soft flocs) because when the white water is recycled, these same TiO_2 particles are redistributed on the fines and fibrils of the fibers.

The result is slightly different when clay is to be retained. Clay retention is very sensitive to the presence of fines. Clay is preferentially adsorbed onto the fines rather than onto the fibrils of the fibers. This is probably due to the greater shearing force they experience due to their larger size during sheet formation.

The smaller, spherical TiO_2 particles do not experience such large forces and therefore remain attached to the fibrils. Both TiO_2 and clay are adsorbed upon the fines, but the larger clay particles probably have stronger surface chemical forces than do the smaller TiO_2 particles. It is essential, therefore, to maximize fines retention, especially if clay is used as a filler.

Stock Dilution

The more dilute the headbox stock, the more water there is which will have to be drained from the web. This allows more time for the fines to escape, which reduces retention (36).

Wire Length and Mesh Size

A longer wire allows more time for drainage and thus improves retention. The finer the mesh, the better the filtration and the better the retention (36).

Ion Valence

Walkush and Williams (2) proposed the existence of a critical coagulation concentration (CCC), which is the concentration of polymer needed to achieve a certain level of retention. They hold that, as cation valence increases, CCC decreases. This is consistent with previous discussions, and it is an expected result. The higher the cation valence, the better it would be at electrical layer suppression, and hence, less of the cation would be needed to reach the same level of retention.

IV. Parameter Influenced by Retention

Papermaking Parameters

Improving retention on the wet end of the papermachine has some very important results. The reasons for retention study are found in improving such things as drainage, machine speed, production and formation. With increases in retention come decreases in material costs, energy requirements - especially during drying, and reduced B.O.D. levels in mill effluent. These are important economic results which must be considered and balanced against the cost of implementing a retention improvement program.

Paper Properties

Along with the economic factors listed above, retention of fines and fillers, and their distribution in the sheet itself, are the controlling factors for paper optical and strength properties.

Brightness and opacity are the two main optical properties influenced by retention. Schiesser (5) points out the strong, direct relationship between sheet ash content (retention) and opacity. Increasing retention increases sheet ash content which will generally tend to improve opacity.

Scattering coefficient, absorption coefficient and reflecting surface area are underlying optical properties which are affected by retention. Complete discussions of these three properties and how they are affected by retention are given by Pummer (10, 32) and Robinson (17). Basically, increasing retention means that the filler particles must be flocculated or coagulated, thus reducing the individual particles scattering coefficient and reflecting surface area.

However, as more of the filler is retained in the sheet, opacity increases, up to the point of over-flocculation.

Recycling white water, as most mills now do, can produce opacity gains due to the extra mixing which occurs. Williams (29) states that this mixing tends to break up agglomerated particles and causes them to be more evenly distributed in the sheet. This recycling process must be controlled to prevent the build-up of residual lignin, which is usually associated with the fines fraction, from causing losses in brightness.

One must be careful, too, to be sure that any retention aid added does not hurt brightness because of its inherent color or because it causes discoloration with time (32).

Increased retention can affect sheet strength properties, especially tensile strength. Care must be exercised to maintain good formation. Over flocculation will hurt formation and strength.

V. Retention Aids

A retention aid is considered to be any chemical which is able to form a floc or coagula, change the surface charge characteristics of the fibers and other particles, or act as a chemical bridge between particles of like charge. This definition, as presented by Nelson and Jursich (15) includes the statement that a good retention aid will perform all three of these functions.

Nelson and Jursich (15) list four main classes of retention aids:

- (1) Inorganic Compounds - including alum, sodium aluminate, and activated silica.
- (2) Naturally Occuring Organic Compounds - glues and starches.
- (3) Modified Natural Organic Compounds - modified gums and starches.
- (4) Synthetic Organic Compounds - cationic, non-ionic and anionic water soluble organic compounds.

Alum is one of the oldest retention aids in use today. Adding alum reduces the pH thereby lowering the electronegativity of the fibers and inducing flocculation. Complete discussions of alum are given by Schurz (30) and Strazdin (20).

Measurement of Retention

Many different techniques have been developed over the years to measure and test retention. Probably the oldest is simple hand sheet analysis. The basic drawbacks of this method are its lack of shear and its high dilution. Rogols (12) described a rapid method for determining retention in 1963. It involves preparation of the furnish in a Waring blender and the subsequent filtering in a Buchner funnel.

Two rather recent developments better simulate the actual conditions on a papermachine. One is the mini-drainer retention tester as developed by Werdouschegg (26). The other is the Britt jar or "dynamic retention/drainage tester" as developed by Britt and Unbehend (16). The mini-drainer simulates the retention and drainage

on the fourdrinier wet end. The Britt jar simulates retention due to colloidal forces only, independent of mat formation (27).

The Britt jar will be used for the experimental portion of this report.

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PRESENTATION OF PROBLEM

Throughout the preceeding literature survey the entire area of retention was reviewed and discussed. The various physical and chemical aspects of retention were presented to provide a better, more complete and concise understanding of the entire area of retention.

During the preparation of the literature review, it became apparent that there were some disagreeing and conflicting reports as to the effect of polymer molecular weight on retention and the bridging mechanism. Several unanswered, or inadequately answered questions arose. Does retention increase with increasing polymer molecular weight? Is there an optimum molecular weight for each particular polymer in every system or must each polymer be evaluated in every different system? Is molecular weight or charge distribution-charge density the controlling factor in bridging? Does higher molecular weight give increased shear stability?

The primary goal of this experimental work was to determine the effects of polymer molecular weight on colloidal retention and the bridging mechanism. Through careful selection and combination of the various chemical and mechanical aspects of the experiment, it may be possible to illuminate some of these other questions and there by provide a firm basis for further studies.

EXPERIMENTAL

EXPERIMENTAL DESIGN

The experiment was completely randomized in order to avoid any bias which would be inadvertently introduced by the experimenter.

Details of this randomization can be found in Appendicies I and II.

The dynamic retention/drainage jar was the apparatus utilized to study two cationic and two non-ionic additives at two different levels of shear. A low and a high molecular weight additive was chosen in each group. The low molecular weight cationic retention aid was of the polyethylene imine type. The high molecular weight cationic retention aid was of the polyacrylamide type. Both the non-ionic additives are termed "bridging agents" and are polyethylene oxides.

Use of these non-ionic and ionic, high and low molecular weight additives makes it possible to study the effects of molecular weight and charge separately. Combination of the various chemicals at different levels of addition and different ratios will provide insight into synergistic effects. By varying the level of shear, its effect on the different chemical combinations can be observed.

EXPERIMENTAL DEVELOPMENT

Before any experimental work was begun, it was necessary to acquaint myself with the operation of the dynamic retention/drainage jar. Many preliminary runs were made in an attempt to become consistent and replicable with the results. Several adjustments in the experimental procedure were made in an attempt to fine tune the experiment.

During the trial runs it became evident that the original rpm values of 750 rpm and 1500 rpm did not provide sufficient spread in the data results. The lower rpm level was reduced to 600 rpm.

Another problem was encountered with the master batch agitation. The problem was insufficient mixing due to an inadequately sized stirrer. The problem was remedied when a larger agitator was installed.

The system originally employed for the weighing of the filtrate from the jar also provided some difficulty. It was originally planned to drain the filtrate into an 80 ml weighing jar, evaporate off the water and determine the weight of the residue by difference. Part of the problem lie in trying to determine a very small weight by taking the difference obtained by subtracting two relatively large weights. This procedure did not give consistent, reproducible weights. It was necessary to employ pre-dried and weighed filter paper and a dual Buchner funnel arrangement to obtain the weight of the filtrate. The filter paper was placed in a light, air tight plastic container of known weight before it was removed from the oven. Subsequent moisture pick-up by the filter paper and/or filtrate residue was greatly retarded. This allowed for rapid, accurate determination of the filtrate weight by the difference between much smaller weights, thus increasing the accuracy of the result.

Several modifications of the dynamic retention/drainage jar were also deemed necessary after several practice runs were completed.

First, baffles were installed at 120° intervals around the interior of the jar. These were installed in an effort to reduce the variability caused by vortex formation, especially at high shear rates. The baffles measured 14.0 cm x 1.3 cm x 0.6 cm.

It became immediately apparent that as soon as stock was introduced into the jar, some of the fines material was carried through the

screen by the water and into the drainage chamber below. A three way glass valve was installed to replace the pinch clamp arrangement of the original jar. Attached to one side of the valve was a positive air pressure of approximately 6 oz/in^2 (.40 psi). This is just enough pressure to offset the pressure exerted by the liquid level in the jar ($p = h \rho$). The reduction and control to such a low pressure was accomplished by using a series of 5 valves and one actuator. See Appendix III for pictures.

Before the stock was placed in the jar, the positive air pressure was introduced to the underside of the wire through the three-way valve. The stock was then placed in the jar. By subsequent observation just before and during the stock drainage, it could be clearly noted that no drainage took place until the air pressure was removed and the drainage tube was exposed to atmospheric pressure.

This modification tended to accomplish several things. It served to keep all the fine material above the wire in the upper level of the jar where it could be properly exposed to both the applied shear and the applied chemicals. This modification, in my opinion, made the dynamic retention/drainage jar more closely approximate the dynamic conditions encountered on the wire just after the slice.

EXPERIMENTAL PROCEDURE

The only variables which were directly altered during the course of the experiment were molecular weight, shear and level of addition. All the other variables discussed in the preceeding sections will be

assumed constant (pH, temperature, zeta potential), controlled so they are constant (refining, time of exposure, order of addition, water type, carboxyl content, filler type, stock dilution, ion valence), or assumed unsequential or non-existent (basis weight, machine mechanical action, wire length, wire mesh size).

The following is an outline of the procedure used. A more detailed procedure and the required calculations can be found in Appendix I.

Pulp was prepared in a 50-50 ratio of hardwood bleached kraft to softwood bleached kraft. A laboratory scale beater was utilized to reduce the freeness to 350 ml CS freeness. 25% TiO_2 was supplied to the mixture and allowed to mix in thoroughly with the weights removed from the beater. The pulp was then centrifuged in muslin cloth to reduce the loss of fines and filler and allowed to air dry for three weeks.

The dynamic retention/drainage jar was the basic apparatus used in this experiment. A 76μ m, 200 mesh 125P screen was used. The function and use of this equipment has been described earlier in this report and can also be found in detail in Appendix I.

The fines content was then determined using the fractionation procedure outlined in Appendix I.

Master batches of pulp of predetermined consistency were prepared from the air dried stock using a Tappi disintegrator for redispersion.

The master batches of known consistency provided samples which were subsequently introduced into the dynamic retention/drainage jar. Chemicals were added and drainage was induced after predetermined intervals.

The filtrate was weighed and filtered on a filter paper of known weight in a Buchner funnel. The filter paper with the filtrate solids deposited on its surface was dried in a fast drying circulating oven. The dry weight of the filtrate solids was determined using a Mettler balance to within $\pm 5 \times 10^{-4}$ grams.

Retention values were determined for each combination of chemicals at 600 rpm and 1500 rpm. Each trial was replicated three times.

The sequence of replication was determined using a random number table (39), with each replication being assigned a three digit number (since the total number of runs would be 216, a three digit number was required). For the general outline of the experiment see Table IA in Appendix I.

Retention values were calculated, Table IB in Appendix I, with the graphs and tables presented later in this paper based on these values. It should be noted that the enclosed values in Table IA were statistically eliminated using the Q test for elimination of data. The averages shown in Table IB are based upon the remaining data points.

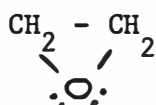
The additives used to improve retention in this experiment are as follows: a low molecular weight cationic polyethylene imine (LRA), a high molecular weight cationic hydrolyzed polyacrylamide (HRA), a low molecular weight (approximately 900,000 m.w) non-ionic polyethylene oxide (LBA), and a high molecular weight (approximately 4,000,000 m.w.) non-ionic polyethylene oxide (HBA).

The chemical and physical properties of the former two additives have been fully documented and reported. They are discussed in (15).

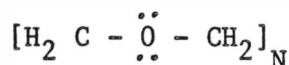
The latter two chemicals are rather new, water soluble resins developed by the Union Carbide Corporation (40).

In this study they are the "bridging agent" which theoretically provides a bridge between fibers or between fibers and fines in order to increase retention. Their use will allow study of the bridging mechanism, independent of ionic forces, due to their non-ionic nature. This may also lead to some understanding of the molecular weight versus charge distribution-charge density relationship, if one does indeed exist.

These resin polymers of ethylene oxide, the structures of which are shown below, have hydrogen bonding capability at the oxygen site. (This should be expected since they are polyethers) (40). Theoretically, they should hydrogen bond with cellulose to form intermolecular



ethylene oxide



polyethylene oxide

links which will improve the retention of fine material (including cellulose fines, fillers, and other additives).

Polyethylene oxide is instantly wetted by water (due to its hydrogen bonding ability) and should be dispersed with high shear for prolonged periods. If high shear is applied for extended periods, degradation of the polymer chain may result.

Even though they are readily wetted by water during dispersion, they resist the pickup of atmospheric moisture even at high humidity levels. They have the capability of reducing the friction associated with the fluid in which they are dispersed. Since they are non-ionic they are more tolerant of dissolved salts than are ionic polymers. These resins are also non-toxic.

EXPERIMENTAL IMPROVEMENT

If there was time to adjust and modify this experimental procedure even more than it has already been modified, several more things would be changed.

First of all, the high shear rate of 1500 rpm would be adjusted down to 1000 rpm. With the installation of the baffles, the shear in the jar was greatly increased at any given rpm. The level of 1500 rpm was chosen before the baffles were installed and failure to recognize this problem lead to very low values of retention at the high shear rate.

Secondly, the chemical solutions of the retention aids and the bridging agents should be used as rapidly as possible after they are prepared. The solutions should be replaced after 48 hours. This 48 hour figure is not based on known facts, but is only intended as an approximate maximum storage time. This would reduce any error due to possible polymer degradation caused by prolonged solution storage.

The solutions in this experiment were discarded after seven days. The longer storage time was necessitated by the limited time allowed

for actual experimental work. In order to facilitate completion of all planned work, it was necessary to prepare larger quantities of the solutions which meant they would have to remain in liquid storage longer than desired.

Thirdly, the master batches of pulp solution would be kept at one temperature. For the reasons mentioned above, the master batches were moved to a cooler than room temperature location when they were not in use. This was done to retard any bacteriological attack on the pulp. The use of chemical preservatives was considered. However, it was desired to study the system with as little interference from outside sources as possible so no preservative was added. It was found that the master batches could be used up rapidly enough and they were kept at low enough consistency so that they could have been stored at room temperature for a week or so without any fear of degradation.

RESULTS AND DISCUSSION

The results of this experiment will be discussed and presented on the basis of maximum retention obtained, retention relative to level of addition, loss in retention due to shear and the percent improvement in retention relative to level of addition. The results will be discussed as they relate to one another within a group under certain conditions and as various groups compared to each other.

OPTIMUM RETENTION

Low Shear

Figures 6 and 7 show graphically a summary of the results of this study obtained at 600 rpm for the addition of both low molecular weight bridging agent (LBA) and high molecular weight bridging agent (HBA) to low molecular weight cationic retention aid (LRA, Figure 6) and high molecular weight cationic retention aid (HRA, Figure 7) at various levels of addition for both the bridging agents and the retention aids (0 lbs/ton, 0.75 lbs/ton, 1.5 lbs/ton).

Referring to Figure 6, maximum retention was obtained with the combinations of 0.75 LRA + 1.5 LBA and 0.75 LRA + 0.75 HBA. Figure 7 shows that retention was maximized with the combinations of 1.5 HRA + 1.5 LBA and 1.5 HRA + 1.5 HBA.

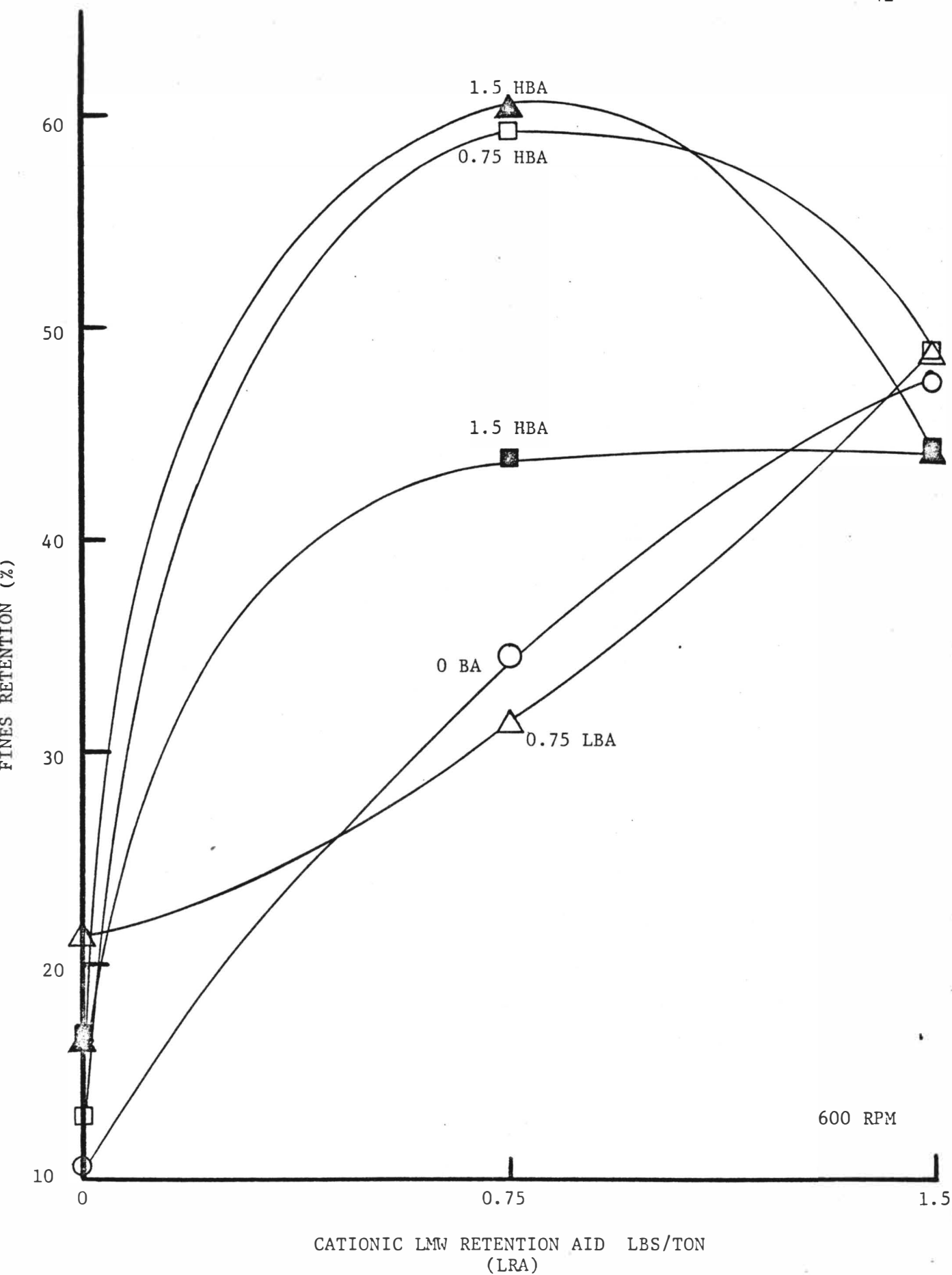


FIGURE 6

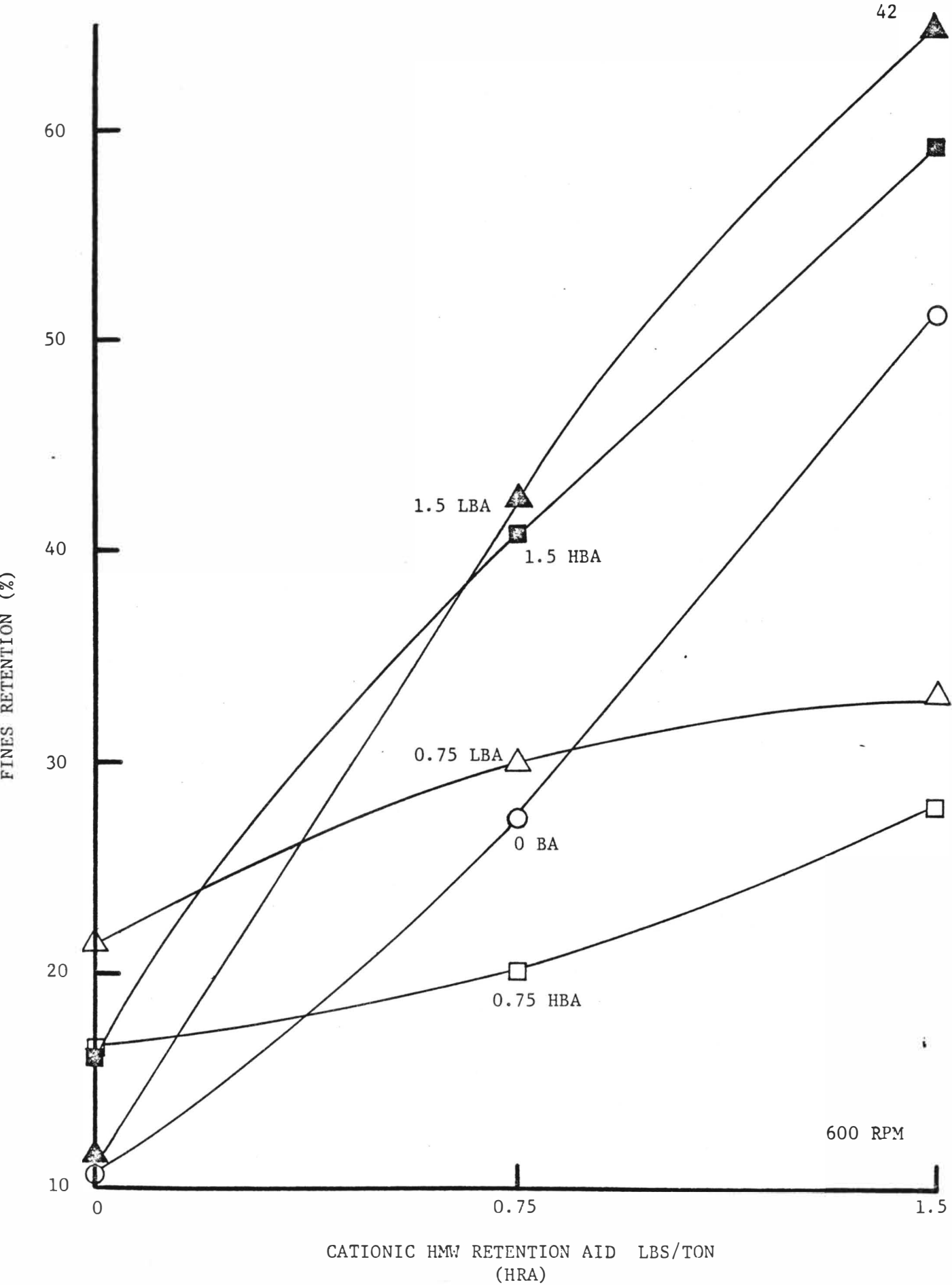


FIGURE 7

High Shear

Turning to Figures 8 and 9 we see the results of these same combinations at 1500 RPM.

Figure 8 shows that optimum retention was obtained with the combinations 1.5 LRA + 1.5 LBA and 1.5 LRA + 0.75 HBA.

When the bridging agents were combined with the HRA, the results shown in Figure 9 were obtained. Here, maximum retention resulted when 0.75 HRA and 1.5 LBA were combined or when 0.75 HRA and 0.75 HBA were combined.

These optimum conditions for both shear rates are shown in Table III.

TABLE III
MAXIMUM RETENTION AT 600 AND 1500 RPM

<u>Relative Rank</u>	<u>600 RPM</u>	<u>% Ret.</u>	<u>Relative Rank</u>	<u>1500 RPM</u>	<u>% Ret.</u>
2	0.75 LRA + 1.5 LBA	60.3	2	1.5 LRA + 1.5 LBA	25.2
3	0.75 LRA + 0.75 HBA	59.3	1	1.5 LRA + 0.75 HBA	32.3
1	1.5 HRA + 1.5 LBA	64.8	3	0.75 HRA + 1.5 LBA	22.4
4	1.5 HRA + 1.5 HBA	58.2	4	0.75 HRA + 0.75 HBA	21.5

The pattern which develops in this data is clear. The best retention occurs at both levels of shear when high and low molecular weights are combined. At both shear levels, in 3 out of the 4 cases it takes more LBA than HBA in combination with either RA to obtain approximately the same level of retention.

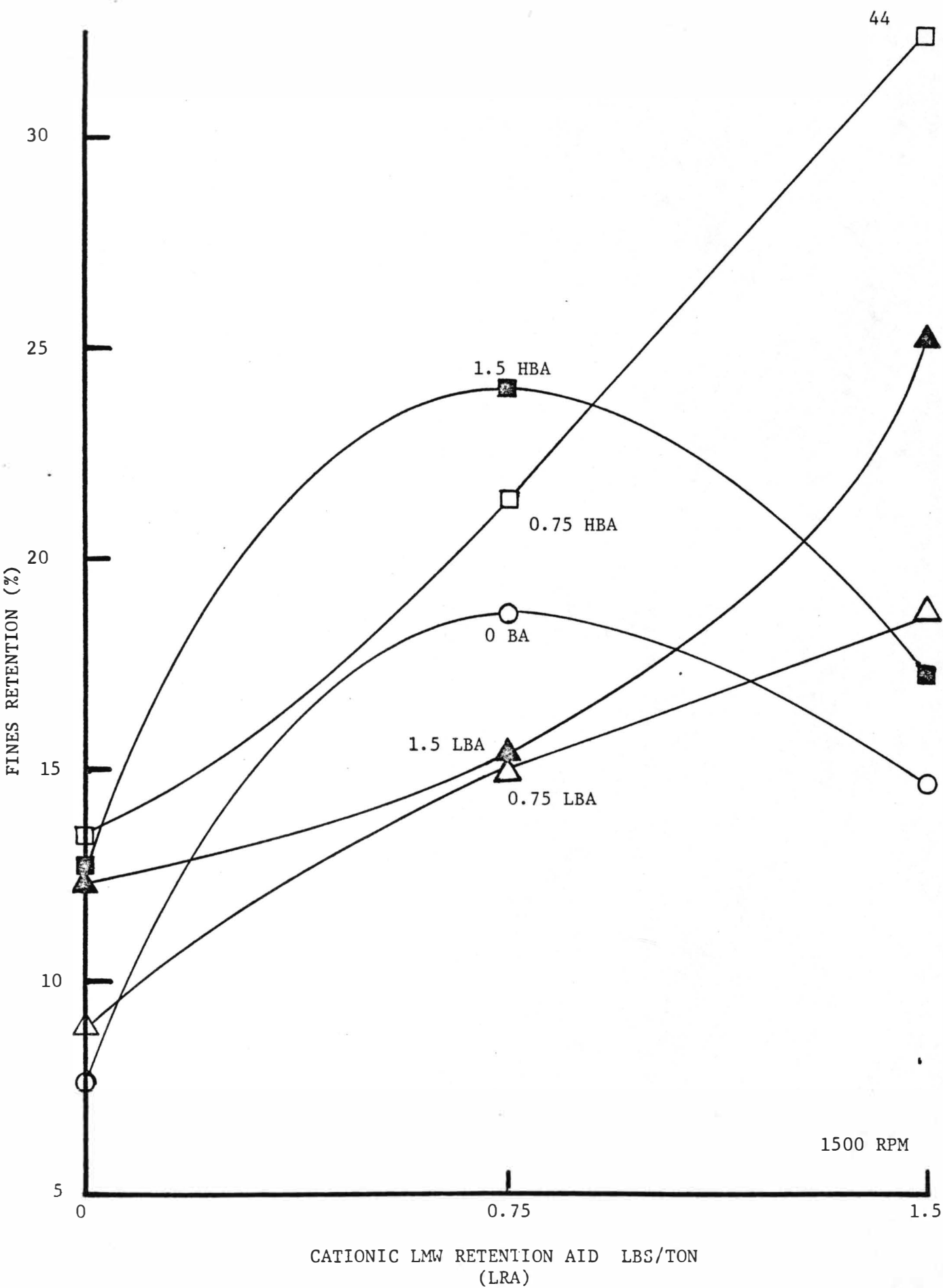


FIGURE 8

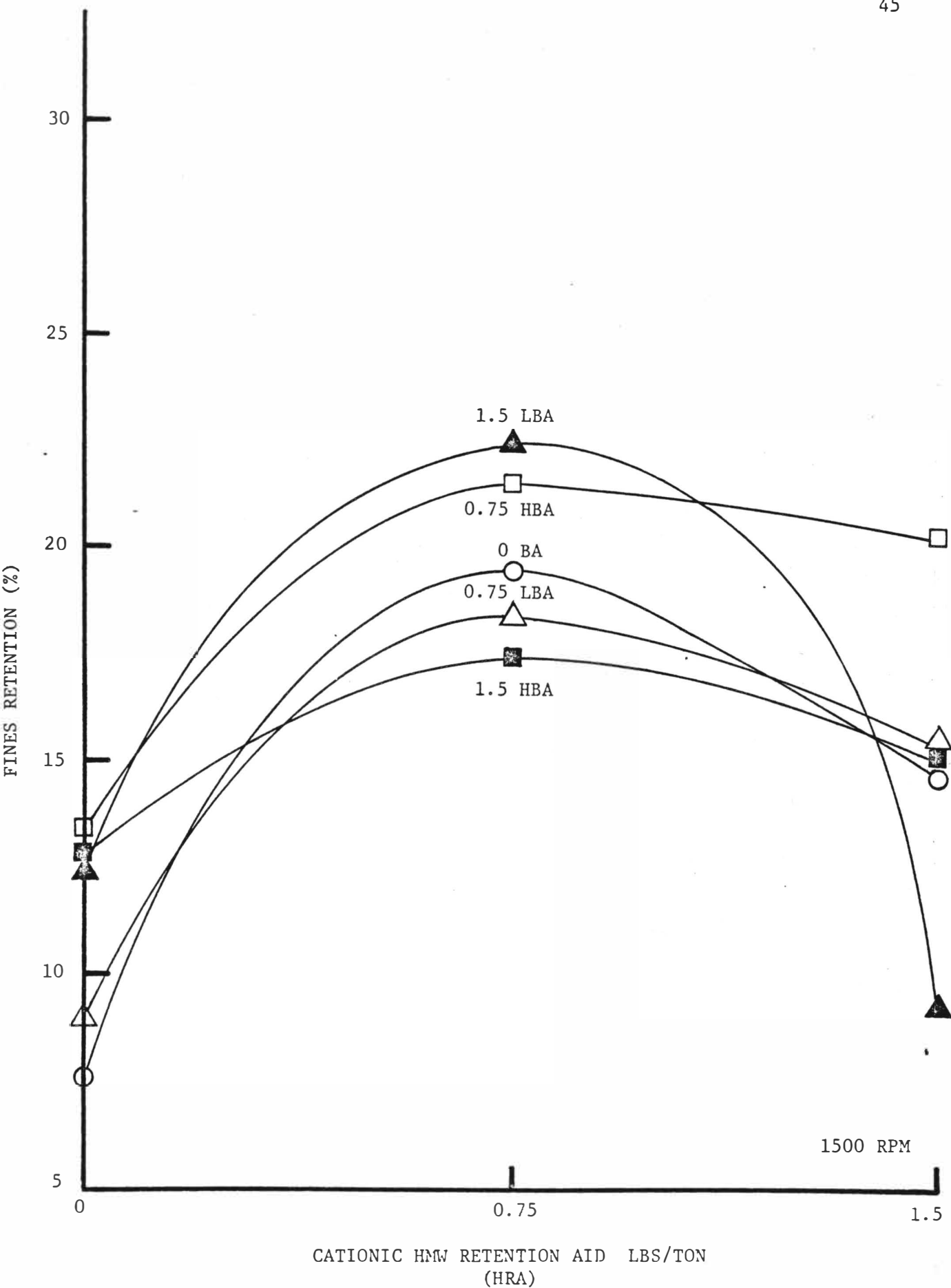


FIGURE 9

RETENTION AND LEVEL OF ADDITION

Low ShearTotal Level of Addition 0.75 lbs/ton

As shown in the first part of Table IV the bridging agents alone did not increase retention significantly, although some small increases did occur over the control group (no additive, 10.6% retention). It is interesting to note that for both the retention aids and the bridging agents, the lower molecular weight chemicals gave slightly better retention than did the higher molecular weight chemicals.

Total Level of Addition 1.5 lbs/ton

The trend observed at the 0.75 lbs/ton total addition level described above was reversed when the level of addition increased to 1.5 lbs/ton. The higher molecular weight chemicals gave slightly higher retention than did the lower molecular weight chemicals.

Replacing 50% of the RA with LBA caused a loss in retention of about 35%. However, when 50% of the LRA was replaced with HBA, a retention increase of 25% resulted.

When 50% of the HRA was replaced with LBA, a 41% drop in retention resulted. Similar replacement with HBA caused a 60% drop in retention.

Total Level of Addition 2.25 lbs/ton

At this level of addition, there were two possible ways to obtain the required 2.25 lbs/ton level of addition. These two possibilities are shown in Table IV.

TABLE IV
RETENTION AND LEVEL OF ADDITION 600 RPM

<u>LRA</u>	<u>LBA</u>	<u>%Ret.</u>	<u>LRA</u>	<u>HBA</u>	<u>%Ret.</u>	<u>HRA</u>	<u>LBA</u>	<u>%Ret.</u>	<u>HRA</u>	<u>HBA</u>	<u>%Ret.</u>
<u>TOTAL LEVEL OF ADDITION 0.75 LBS/TON*</u>											
0	0.75	21.4	0	0.75	16.7	0	0.75	21.4	0	0.75	16.7
0.75	0	34.4	0.75	0	34.4	0.75	0	27.3	0.75	0	27.3
<u>TOTAL LEVEL OF ADDITION 1.5 LBS/TON*</u>											
0	1.5	11.4	0	1.5	16.5	0	1.5	11.4	0	1.5	11.4
1.5	0	47.6	1.5	0	47.6	1.5	0	51.1	1.5	0	51.1
0.75	0.75	30.8	0.75	0.75	59.3	0.75	0.75	30.1	0.75	0.75	20.2
<u>TOTAL LEVEL OF ADDITION 2.25 LBS/TON*</u>											
0.75	1.5	60.3	0.75	1.5	43.9	0.75	1.5	42.6	0.75	1.5	40.9
1.5	0.75	48.4	1.5	0.75	48.1	1.5	0.75	33.2	1.5	0.75	27.9
<u>TOTAL LEVEL OF ADDITION 3.0 LBS/TON*</u>											
1.5	1.5	44.0	1.5	1.5	44.1	1.5	1.5	64.8	1.5	1.5	58.2

*Base retention at 0 lbs/ton total addition level = 10.6%.

In 3 out of 4 cases, 50% replacement of the RA with BA, be it LBA or HBA, caused increases in retention of from 26% to 47%. 50% replacement of the HRA with HBA caused the largest increase, 47%. 50% replacement of the HRA by the LBA gave 28% higher retention. 50% replacement of the LRA with HBA gave an unexplainable decrease in retention of 9%. Finally, replacing 50% of the LRA with LBA gave a 26% increase in retention.

Total Level of Addition 3.0 lbs/ton

At this level of addition, the best results were obtained when 1.5 HRA and 1.5 LBA were combined. The next best results were with 1.5 HRA and 1.5 HBA. The combination of 1.5 LRA + 1.5 HBA was only slightly better than 1.5 LRA + 1.5 LBA.

High Shear

Total Level of Addition 0.75 lbs/ton

The results observed under these same conditions at the low shear level did not reoccur when the shear rate was increased to 1500 rpm, Table V. Under high shear the respective higher molecular weight chemicals gave slightly better retention than did the low molecular weight chemicals. Again, the bridging agents inability to act alone is shown. The retention values obtained were not significantly different from those obtained when no retention aid or bridging agent was added.

Total Level of Addition 1.5 lbs/ton

At this total level of addition, about the same results were observed as at the low level of shear. The HBA gave just slightly better retention than the LBA. The LRA and the HRA gave virtually the same retention.

Upon 50% replacement of the RA with BA, the exact opposite occurred from what took place at the same level under low shear. In all four cases, 50% replacement of RA with BA caused increases in retention. The increases ranged from 2% for the combination of LRA + LBA to 47% for the combination HRA + HBA. Combining LRA + HBA gave 46% improvement in retention while the combination of HRA and LBA gave a 25% increase in retention.

This is exactly the opposite trend from what was observed at 600 rpm except for the LRA + HBA combination, which gave a 25% increase in retention.

Total Level of Addition 2.25 lbs/ton

At high shear and this level of addition, the results obtained are again exactly opposite in 3 out of 4 cases, to those results obtained at the low shear level. Instead of 50% replacement of the RA with BA causing an increase in retention as it did at the low shear level, it caused a reduction in retention in 3 out of the 4 cases. The percent reductions ranged from 14% for the HRA + HBA to 25% for the LRA + HBA. The combination of LRA + LBA gave a reduction in retention of 15%.

TABLE V
RETENTION AND LEVEL OF ADDITION 1500 RPM

<u>LRA</u>	<u>LBA</u>	<u>%Ret.</u>	<u>LRA</u>	<u>HBA</u>	<u>%Ret.</u>	<u>HRA</u>	<u>LBA</u>	<u>%Ret.</u>	<u>HRA</u>	<u>HBA</u>	<u>%Ret.</u>
<u>TOTAL LEVEL OF ADDITION 0.75 LBS/TON*</u>											
0	0.75	8.9	0	0.75	13.4	0	0.75	8.9	0	0.75	13.4
0.75	0	18.7	0.75	0	18.7	0.75	0	19.4	0.75	0	19.4
<u>TOTAL LEVEL OF ADDITION 1.5 LBS/TON*</u>											
0	1.5	12.4	0	1.5	12.7	0	1.5	12.4	0	1.5	12.7
1.5	0	14.7	1.5	0	14.7	1.5	0	14.6	1.5	0	14.6
0.75	0.75	15.0	0.75	0.75	21.4	0.75	0.75	18.3	0.75	0.75	21.5
<u>TOTAL LEVEL OF ADDITION 2.25 LBS/TON*</u>											
0.75	1.5	15.4	0.75	1.5	24.1	0.75	1.5	22.4	0.75	1.5	17.4
1.5	0.75	18.2	1.5	0.75	32.3	1.5	0.75	15.4	1.5	0.75	20.2
<u>TOTAL LEVEL OF ADDITION 3.0 LBS/TON*</u>											
1.5	1.5	25.2	1.5	1.5	16.0	1.5	1.5	9.2	1.5	1.5	15.1

*Base retention at 0 lbs/ton total addition level = 7.6%.

The differing group which gave an increase in retention when 50% RA was replaced with BA was the combination of HRA + LBA. The percent increase was substantial, 45%. It is worth noting that this is not the same group that gave the contrary results in this section at the low shear rate. That group was the combination of LRA + HBA. It is interesting to note, however, that in both cases the differing group was a combination of low molecular weight with high molecular weight.

Total Level of Addition 3.0 lbs/ton

Once again, under the influence of the high shear condition, the results were opposite to those obtained at the low shear level. Where as before the best combinations were HRA + HBA and HRA + LBA, under high shear the best combinations were found to be LRA + LBA and LRA + HBA. In retrospect, these two combinations gave the lowest results at the low shear level.

At the high shear level, the lowest results were obtained with the combination HRA + LBA and HRA + HBA. As pointed out earlier, these two combinations gave the best retention at the low shear rate.

RETENTION REDUCTION DUE TO INCREASED SHEAR

In order to study the shear stability of the various combinations of chemicals, the percent reduction in retention was calculated for each combination of chemicals as shown in Table IIIA, Appendix II.

These values were then converted to percent reduction in retention at the various total levels of addition.

It was at this point that a problem became evident. It became clear that the combinations of chemicals which had low initial retention values would give lower percent reduction in retention values than combinations of chemicals which had higher initial retention. In an attempt to normalize the data and remove this bias, a quantity called the shear reduction coefficient (SRC) was defined as follows. The SRC is the percent reduction in retention per unit of initial retention at the low shear level. In equation form this becomes:

$$\text{SRC} = \frac{\% \text{ Reduction in Retention}}{\% \text{ Retention @ Low Shear}} \quad (4)$$

$$\text{SRC} = \frac{\% \text{ Retention @ Low Shear} - \% \text{ Retention @ High Shear} \times 100}{(\% \text{ Retention @ Low Shear})^2} \quad (5)$$

Keeping this definition in mind, it is important to remember that this is a purely empirical relationship. No linearity is assumed or implied. The purpose of the SRC definition is as a tool for explaining the results obtained.

Referring to Table VI, the results of the conversion from percent reduction in retention to the SRC can be examined. It should be noted that the lower the SRC the more shear stability that is provided by the respective chemical combinations.

Total Level of Addition 0.75 lbs/ton

At this level of addition the HRA gave greater stability towards shear than the LRA (lower SRC). The HBA similarly outperformed the LBA.

Total Level of Addition 1.5 lbs/ton

When the total amount of chemical was doubled, the HRA and the LRA performed about the same (1.40 vs 1.45). The results of the HBA vs the LBA were somewhat clouded by the negative value of the SRC for the LBA (an actual increase in retention upon increasing shear). This may have been caused by experimental error as the actual retention values were low, thereby increasing the possibility of error. The trend, however, would indicate that the LBA worked better than the HBA.

When 50% of the LRA was replaced by LBA the SRC increased but not significantly. When the same replacement was made with HBA the SRC decreased, indicating greater stability was provided by the HBA. This trend repeated itself when 50% of the HRA was replaced with HBA but again a negative SRC clouds the result. As before, when 50% of the RA, this time HRA, was replaced with LBA no significant change occurred but this time it was only a slight decrease in the SRC.

Total Level of Addition 2.25 lbs/ton

50% replacement of the LRA with LBA gave no appreciable change in the SRC. However, this same replacement with HBA caused the SRC to decrease significantly. Subsequent replacement of 50% of the HRA with LBA caused considerable reduction in the SRC but replacement with HBA caused the SRC to increase.

Total Level of Addition 3.0 lbs/ton

At this level of addition, the combination of LRA + LBA performed the best. The other three groups were about equal in their resistance to retention reduction with increasing shear.

TABLE VI
RETENTION REDUCTION DUE TO INCREASED SHEAR
BASED ON SHEAR REDUCTION COEFFICIENT*

<u>LRA</u>	<u>LBA</u>	<u>SRC</u>	<u>LRA</u>	<u>HBA</u>	<u>SRC</u>	<u>HRA</u>	<u>LBA</u>	<u>SRC</u>	<u>HRA</u>	<u>HBA</u>	<u>SRC</u>
<u>TOTAL LEVEL OF ADDITION OF 0.75 LBS/TON</u>											
0	0	2.67	0	0	2.67	0	0	2.67	0	0	2.67
0	0.75	2.73	0	0.75	1.18	0	0.75	2.73	0	0.75	1.18
0.75	0	1.32	0.75	0	1.32	0.75	0	1.06	0.75	0	1.06
<u>TOTAL LEVEL OF ADDITION 1.5 LBS/TON</u>											
0	1.5	(0.77)	0	1.5	1.39	0	1.5	(0.77)	0	1.5	1.39
1.5	0	1.45	1.5	0	1.45	1.5	0	1.40	1.5	0	1.40
0.75	0.75	1.66	0.75	0.75	1.08	0.75	0.75	1.30	0.75	0.75	(0.32)
<u>TOTAL LEVEL OF ADDITION 2.25 LBS/TON</u>											
0.75	1.5	1.24	0.75	1.5	1.03	0.75	1.5	1.11	0.75	1.5	1.40
1.5	0.75	1.29	1.5	0.75	0.68	1.5	0.75	1.61	1.5	0.75	(0.99)
<u>TOTAL LEVEL OF ADDITION 3.0 LBS/TON</u>											
1.5	1.5	0.97	1.5	1.5	1.44	1.5	1.5	1.32	1.5	1.5	1.27

*SRC = $\frac{\% \text{ Reduction in Retention}}{\% \text{ Retention @ Low Shear}}$

*SRC = $\frac{\% \text{ Retention @ Low Shear} - \% \text{ Retention @ High Shear}}{(\% \text{ Retention @ Low Shear})^2} \times 100$

PERCENT IMPROVEMENT IN RETENTION

Low Shear

Before discussing the results, it is important to note that the percent improvement figures shown in Table VII and VIII are the percent improvement relative to the 0 lbs/ton additive level. The results as obtained from the experiment can be found in Appendix II, Tables VA and VIA.

Total Level of Addition 0.75 lbs/ton

The figures in Table VII show that the LRA gave a significantly better percent increase in retention than did the HRA. The same trend was observed for the bridging agents. The LBA had higher percent improvement than did the HBA.

Total Level of Addition 1.5 lbs/ton

When the level of addition was increased to 1.5 lbs/ton the results were opposite from what occurred at 0.75 lbs/ton.

In this case the HRA gave slightly higher percent improvement than did the LRA. The HBA also gave higher percent improvement than did the LBA.

When 50% of the LRA was replaced by LBA the percent improvement was lower than with just the LRA alone. However, this same replacement with HBA resulted in a higher percent increase than with LRA alone.

Replacing 50% of the HRA with either LBA or HBA caused lower percent improvement than with just the HRA alone.

TABLE VII

PERCENT IMPROVEMENT IN RETENTION* 600 RPM

<u>LRA</u>	<u>LBA</u>	<u>% Ret.</u>	<u>LRA</u>	<u>HBA</u>	<u>% Ret.</u>	<u>HRA</u>	<u>LBA</u>	<u>% Ret.</u>	<u>HRA</u>	<u>HBA</u>	<u>% Ret.</u>
<u>TOTAL LEVEL OF ADDITION 0.75 LBS/TON</u>											
0	0.75	102	0	0.75	58	0	0.75	102	0	0.75	58
0.75	0	224	0.75	0	224	0.75	0	158	0.75	0	158
<u>TOTAL LEVEL OF ADDITION 1.5 LBS/TON</u>											
0	1.5	8.0	0	1.5	57	0	1.5	8.0	0.	1.5	57
1.5	0	349	1.5	0	349	1.5	0	382	1.5	0	382
0.75	0.75	190	0.75	0.75	459	0.75	0.75	184	0.75	0.75	91
<u>TOTAL LEVEL OF ADDITION 2.25 LBS/TON</u>											
0.75	1.5	469	0.75	1.5	314	0.75	1.5	302	0.75	1.5	286
1.5	0.75	356	1.5	0.75	354	1.5	0.75	213	1.5	0.75	163
<u>TOTAL LEVEL OF ADDITION 3.0 LBS/TON</u>											
1.5	1.5	315	1.5	1.5	316	1.5	1.5	511	1.5	1.5	449

*Based on the 0.0 level of addition retention of 10.6%.

Total Level of Addition 2.25 lbs/ton

At this level of addition, 50% replacement of the LRA with LBA increased the percent improvement over what it was with the LRA alone, contrary to what occurred at the previous level.

When 50% of the LRA was replaced with HBA the percent improvement dropped, also contrary to what occurred at the previous level.

The results obtained for 50% replacement of HRA with BA are also contrary to what occurred at the previous level of addition. Replacing 50% of the HRA with either LBA or HBA caused the percent improvement to increase over the level obtained before replacement.

Total Level of Addition 3.0 lbs/ton

The combinations consisting of HRA + LBA and HRA + HBA gave higher percent improvement than the LRA + LBA and LRA + HBA combinations.

High ShearTotal Level of Addition 0.75 lbs/ton

Contrary to what occurred at the low shear level, the HRA and the HBA gave higher percent improvement than did the LRA and the LBA respectively. See Table VIII. This may tie in with the results discussed earlier in regards to the SRC. It was pointed out that the HRA and the HBA had lower (better) SRC values than did the LRA and LBA. This may explain why the percent improvement was better for the HRA and the HBA compared to the LRA and the LBA.

Total Level of Addition 1.5 lbs/ton

At this level of addition the HRA gave slightly higher percent improvement than did the LRA but the difference could not be considered significant.

The percent improvements for the HBA and LBA were virtually identical.

Replacement of 50% of the LRA with LBA resulted in virtually no change in percent improvement. When HBA was used for this replacement, a significant increase in the percent improvement resulted.

This same result also occurred when 50% of the HRA was replaced with LBA and then with HBA.

Total Level of Addition 2.25 lbs/ton

In all cases of 50% RA replacement by BA except when HRA was replaced with LBA, the percent improvement decreased.

Total Level of Addition 3.0 lbs/ton

The best performing combination at this level was the LRA + LBA. This is again the same trend observed in the SRC mentioned earlier.

The LRA + HBA combination had approximately the same value for percent improvement as the combination HRA + HBA. The lowest percent improvement occurred with HRA + LBA.

TABLE VIII

PERCENT IMPROVEMENT IN RETENTION* 1500 RPM

<u>LRA</u>	<u>LBA</u>	<u>% Ret.</u>	<u>LRA</u>	<u>HBA</u>	<u>% Ret.</u>	<u>HRA</u>	<u>LBA</u>	<u>% Ret.</u>	<u>HRA</u>	<u>HBA</u>	<u>% Ret.</u>
<u>TOTAL LEVEL OF ADDITION 0.75 LBS/TON</u>											
0	0.75	17	0	0.75	76	0	0.75	17	0	0.75	76
0.75	0	146	0.75	0	146	0.75	0	155	0.75	0	155
<u>TOTAL LEVEL OF ADDITION 1.5 LBS/TON</u>											
0	1.5	63	0	1.5	67	0	1.5	63	0	1.5	67
1.5	0	93	1.5	0	93	1.5	0	92	1.5	0	92
0.75	0.75	97	0.75	0.75	182	0.75	0.75	141	0.75	0.75	183
<u>TOTAL LEVEL OF ADDITION 2.25 LBS/TON</u>											
0.75	1.5	103	0.75	1.5	217	0.75	1.5	194	0.75	1.5	129
1.5	0.75	139	1.5	0.75	325	1.5	0.75	103	1.5	0.75	166
<u>TOTAL LEVEL OF ADDITION 3.0 LBS/TON</u>											
1.5	1.5	232	1.5	1.5	110	1.5	1.5	21	1.5	1.5	99

*Based on the 0.0 level of addition retention of 7.6%.

SUMMARY AND CONCLUSIONS

Now that all the results have been presented and discussed, a general overall summary will be included here to try and show the trends and interrelations between all respective groups. Inspection of these comparisons in tabular form will allow general conclusions to be drawn based upon the unique characteristics within this particular system. It is not the intention of this author to imply that the conclusions reached here will apply to every other situation encountered. Rather, these conclusions should be used as a basis for further experimentation to try to relate the findings here to other systems.

OPTIMUM RETENTION

The results presented in Table III show a clear trend. At both levels of RA addition, it requires less HBA than LBA to achieve approximately the same level of retention. Table III also shows that the highest retention will occur when high and low molecular weights are combined.

It can also be seen that when going from the low shear level to the high shear level, the amount of LRA had to be increased to achieve maximum retention while the amount of HRA could be reduced.

Put another way, at the low level of shear, less LRA is needed to achieve maximum retention than HRA. At the high shear level, less HRA is needed to achieve maximum retention.

In conclusion it can be said that for this system, the LRA is more effective than the HRA at low shear. At high shear the HRA is more effective than the LRA. In general, the HBA is more effective than the LBA at either level of shear.

RETENTION AND LEVEL OF ADDITION

Total Level of Addition 0.75 lbs/ton

The bridging agents alone do not work very well at either level of shear. At the low shear level the low molecular weight additives worked better than the high molecular weight additives. The opposite was true at the high level of shear.

Total Level of Addition 1.5 lbs/ton

At the low shear level, replacing 50% of the RA with BA caused retention to drop in 3 out of 4 cases. At the high shear level the same replacement caused retention to increase in all cases.

Total Level of Addition 2.25 lbs/ton

At the low shear level, 50% replacement of RA with BA caused retention to increase in 3 out of 4 cases. At the high shear level the same replacement caused retention to decrease in 3 out of 4 cases.

Total Level of Addition 3.0 lbs/ton

At the low shear level, retention was better when the HRA was combined with the bridging agents. When the shear increased to the high

level, the best results occurred when the LRA was combined with the bridging agents.

In general, one can say that the HMW additives performed better than the LMW additives in all cases but one. The reason or reasons for the one contradictory result are unknown. One possible explanation might be a mobility factor. At the low level of addition and the low shear rate, the HMW additives may not mix in as rapidly. Increasing the shear rate may help overcome this as might increasing the level of addition. At the higher level of addition, the extra additive present might help offset the lack of mobility. It must be remembered that this is only a hypothesis suggested to help explain the observed result.

SHEAR RESISTANCE

Over-all it was shown that HMW gave better shear resistance than LMW. The HBA was equal to or better than the LBA in almost all cases. Replacement of either RA with HBA gave greatly increased shear stability in all cases. When LBA was used to replace other RA, shear stability increased in all cases except one, but not nearly as much as when HBA was the replacement chemical.

The HRA was better than the LRA in every case where they were compared alone.

It is the conclusion of this author that molecular weight and charge are both important in bridge formation. The results show that partial replacement of a charged element with an uncharged one can and will give increased retention and increased resistance to retention reduction

caused by increasing shear. This is not to say that bridging does not occur when only cationic constituents are present. It does point out that bridging increases when a non-ionic polymer of high molecular weight is introduced in partial replacement of that cationic constituent.

The observation that the bridging agents alone do little to improve retention adds credibility to this conclusion. This is not to say that molecular weight and charge are equal partners in this phenomenon. That is an area for future study. It does not mean that an extremely high molecular weight charged polymer would take care of both areas. This too is an area for future study.

The fact that the study shows that a HMW cationic polymer in conjunction with a LMW non-ionic polymer can give results similar to those obtained with a LMW cationic polymer and a HMW non-ionic polymer lends support to the above discussed conclusion.

PERCENT IMPROVEMENT IN RETENTION

Low Shear

Here again, just as in the maximum retention results, the LRA gave higher percent improvement than the HRA when used alone. The same is true for the LBA versus the HBA.

When the level of addition increased, this trend reversed itself just as it did in the previous discussion on maximum retention results. Replacement of either RA with BA at a total level of addition of 1.5 lbs/ton reduced the percent improvement in 3 out of 4 cases.

The percent improvement increased in 3 out of 4 cases when 50% of either RA was replaced with BA at a total level of addition of 2.25 lbs/ton.

High Shear

Under the influence of the high shear at a total addition level of 0.75 lbs/ton, the HBA gave better percent improvement than the LBA and the HRA gave slightly better percent improvement than the LRA although the difference was minimal.

About the same trends occurred at the 1.5 lbs/ton total addition level, but the differences observed would be considered unsubstantial. Upon replacement of 50% of either RA with BA, percent improvement increased in all cases.

At the 2.25 lbs/ton total addition level, replacing half of either RA with BA caused a drop in percent improvement in 3 out of 4 cases.

Table IX is a summary of all these results and conclusions. It makes this complicated discussion understandable and shows the remarkable consistency within the results.

GENERAL CONCLUSIONS

1. HMW gives higher retention than LMW except at the low levels of addition and shear.

2. LRA is more effective at producing maximum retention under low shear conditions than HRA.

3. HRA is more effective at producing maximum retention under high shear conditions than LRA.

4. HBA is more effective than LBA at producing maximum retention regardless of shear.

5. HRA gives greater shear stability than LRA.

6. HBA gives greater shear stability than LBA.

7. When combined with either RA, HBA gives greater shear stability than LBA.

8. Bridging does occur and increases with increasing molecular weight to a point.

9. Molecular weight and charge are both important in bridge formation.

TABLE IX

SUMMARY TABLE

Maximum Retention and Level of Addition

<u>Total Level of Addition</u> LBS/TON	<u>600 rpm</u>		<u>1500 rpm</u>	
	<u>(RA, BA)</u>		<u>(RA, BA)</u>	
0.75	LRA > HRA LBA > HBA	0.75 0 0 0.75	HRA > LRA HBA > LBA	0.75 0 0 0.75
1.50	HRA > LRA HBA > LBA More RA is better than equal portions	1.5 0 0 1.5 (1.5 0) (0.75 0.75).	HRA > LRA HBA \approx LBA More RA is better than all RA	1.5 0 0 1.5 (0.75 0.75) (1.5 0)
2.25	More BA is better than more RA	(0.75 1.5) (1.5 0.75).	More RA is better than more BA	(1.5 0.75) (0.75 1.5).
3.00	HRA with BA is best	(1.5 1.5).	LRA with BA is best	(1.5 1.5).

Percent Improvement In Retention

0.75	LRA > HRA LBA > HBA	(0.75 0) (0 0.75)	HRA > LRA HBA > LBA	(0.75 0) (0 0.75)
1.50	HRA > LRA HBA > LBA More RA is better than equal portions	(1.5 0) (0 1.5) (1.5 0) (0.75 0.75).	HRA \approx LRA HBA > LBA More BA is better than all RA	(1.5 0) (0 1.5) (0.75 0.75) (1.5 0).
2.25	More BA is better than more RA	(0.75 1.5) (1.5 0.75)	More RA is better than more BA	(1.5 0.75) (1.5 1.5)
3.00	HRA with BA is best	(1.5 1.5)	LRA with BA is best	(1.5 1.5)

TABLE IX continued

RETENTION REDUCTION DUE TO INCREASED SHEAR
 BASED ON THE SHEAR REDUCTION COEFFICIENT

Total Level
 of Addition
LBS/TON

(RA, BA)

0.75	0.75	0	HRA > LRA
	0	0.75	HBA > LBA
1.5	1.5	0	HRA \approx LRA
	0	1.5	HBA ? LBA
	0.75	0.75	HBA > LBA with LRA; HBA > LBA with HRA
2.25	0.75	1.5	HBA > LBA with LRA; HBA < LBA with HRA
	1.5	0.75	HBA > LBA with LRA; HBA > LBA with HRA
3.0			LRA with LBA is best; LRA + HBA \approx HRA + HBA \approx HRA + HBA

ADDITIONAL EXPERIMENTAL OBSERVATIONS

During the running of the experiment, observations were made and recorded as to the phenomena which occurred. The proceeding discussion is to air these observations in the hope that they may shed some further light on these complex interactions.

FLOCCULATION

Table X shows the observations made on the filtrate taken from the dynamic retention/drainage jar. NF means that no flocculation took place once the applied shear was removed. LF indicates that after several minutes, some settling of flocculated material could be detected, but most of the colloidal material remained suspended. MF means that two distinct portions were formed and settling of the flocculated material occurred after a few minutes. The upper water layer did, however, remain very cloudy. HF indicates that flocculation occurred rapidly after the applied shear was removed. Within this category the liquid layer became relatively clear.

The first three groups (NF, LF, MF) usually required that the filtrate be run back through the filter paper a second or third time before the filtrate was clear. The HF group required only one filtration to provide clear filtrate.

As can be seen from Table X, the bridging agents did not cause the filtrate to flocculate once the applied shear was removed. It

should be noted that the bridging agents did not cause appreciable flocculation after they were added and before the shear was applied.

In general, the introduction of either RA caused flocs to reform after the shear was removed.

DRAINAGE

The bridging agents seemed to slow down the drainage in the Buchner funnel when the filtrate samples were being dewatered. This may have been due to their high molecular weight plugging up the pores of the filter paper. More likely, it was due to their inability to flocculate the colloidal material present and keep it from plugging up the filter paper pores.

FOAMING

Both bridging agents tended to foam quite heavily while under the influence of shear. This foaming tended to increase as the shear rate increased. These characteristics could lead to problems when using these chemicals on a paper machine.

SUGGESTIONS FOR FURTHER RESEARCH

The work and results presented in this paper should provide a sound starting place for several other studies. The work in the area of molecular weight should be expanded through the use of additional

molecular weights to try to determine the optimum molecular weight for a non-ionic polymer in this and other systems.

The effects of shear is another area where the study could be expanded to give future insight into the dynamics of retention.

The order of addition of the various chemicals could be altered to try and determine what effects this will produce.

The time of contact could be altered and its effect determined.

Along these same lines, the time between chemical addition could be studied for its effects.

The level of shear at the time of addition and its duration may provide yet another side from which to approach further study.

TABLE X

ADDITIONAL EXPERIMENTAL OBSERVATIONS

600 rpm							1500 rpm					
LRA			HRA				LRA			HRA		
0	0.75	1.5	0	0.75	1.5		0	0.75	1.5	0	0.75	1.5
LBA												
0	NF	HF	HF	NF	MF	HF	NF	HF	HF	NF	MF	HF
0.75	NF	HF	HF	NF	LF	MF	NF	HF	HF	NF	MF	MF
1.5	NF	HF	HF	NF	MF	MF	NF	HF	HF	NF	LF	HF
HBA												
0	NF	HF	HF	NF	MF	HF	NF	HF	HF	NF	MF	HF
0.75	NF	HF	HF	NF	MF	MF	NF	HF	HF	NF	LF	MF
1.5	NF	HF	HF	NF	MF	MF	NF	HF	HF	NF	LF	MF

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My appreciation goes out to the Union Carbide Corporation for their allowing me to retain their apparatus for so long. I would also like to thank Union Carbide for supplying the bridging agents utilized in this experiment.

I would like to express my gratitude to Dr. Raymond Janes for his patience and helpful insight.

To my typist, who prefers to remain anonymous, go my deepest thanks.

And last, but certainly not least, I would like to thank my research assistant (who also happens to be my wife) for her greatly needed help during the crucial and tedious experimental work.

APPENDIX I

DETAILED EXPERIMENTAL PROCEDURE AND CALCULATIONS

OUTLINE EXPERIMENT

This should include information such as the type and amount of chemicals, mechanical factors such as shear, the number of replications and other pertinent information.

EXPERIMENTAL DESIGN

Layout the experiment as shown in Table IA, Appendix II or in some similar fashion. If it is desired to do the sequence of replication randomly, assign each replication a number and using a random number table, determine the proper sequence.

OBTAIN REQUIRED MATERIALS

This may include chemicals, filter paper, glassware, weighing apparatus, means of chemical addition (syringes, pipets, etc.), and any auxiliary material specific to the particular experiment.

PREPARE PULP FORMULATION

A 50% hardwood kraft - 50% softwood kraft furnish is beaten to a CS freeness of 350 ml. Approximately 25% TiO_2 is added to the

beater with the weights removed to allow the TiO_2 to mix in (42, 43). This pulp is then centrifuged in muslin cloth to remove most of the water. The pulp is then allowed to air dry to 4.920% moisture. De-ionized or distilled water is used throughout the experiment.

PREPARATION OF MASTER BATH

From the air dried pulp, weigh out 99.3 grams of stock and re-disperse it in a Tappi disintegrator with two liters of distilled water after soaking the pulp for one-half hour. Dilute with distilled water to five gallons.

Calculations

$$5 \text{ gallons} \times \frac{3.785 \text{ liters}}{1 \text{ gallon}} = 18.925 \text{ liters} \times \frac{2-500 \text{ ml portions}}{1 \text{ liter}} =$$

37.85 500 ml portions.

Assuming 500 ml in the dynamic retention/drainage jar

@ .5% consistency

$$500 \text{ ml} \times .005 = \frac{2.5 \text{ grams of O.D. fiber}}{500 \text{ ml portion}} \times 37.85 - 500 \text{ ml portions} =$$

94.625 grams of O.D. fiber

94.625 grams of O.D. fiber $\times 1.0492$ = 99.3 grams diluted to 5 gallons.

CONSISTENCY OF MASTER BATCH

Accurately calculate the percent consistency by filtering a weighed quantity (100 ml) of the master batch through a previously weighed filter

paper. Dry the filter paper plus filtrate residue in a fast drying circulating oven. Weigh the dry filter paper and record its weight. Repeat this procedure as many times as necessary to obtain three consecutive runs which agree closely.

$$\text{Percent consistency} = \frac{(\text{Weight of the filter paper plus filtrate}) - \text{Weight of the total sample}}{\text{Weight of the total sample}}$$

$$\frac{(\text{Weight of the filter paper})}{(\text{approximately 100 ml})} \times 100 \quad (6)$$

WET SCREENING

Dilute a portion of the master batch to 0.1% consistency. Take a 500 ml sample of this and accurately determine its weight. Pour the sample into the dynamic retention/drainage jar with the stop cock closed. Add 1.0 ml of dispersing solution to the 500 ml sample. The stock solution of dispersant is made up of equal portions of 2.5% each, Tamol 850, tri-polyphosphate, and sodium carbonate. Set the agitator to 1500 rpm for three seconds, then down to 750 rpm and drain the jar. Add 2.0 ml of dispersing solution to 500 ml of distilled water and pour this into the jar with the stop cock closed. Again set the stirrer to 1500 rpm then 750 rpm and drain as before. Repeat this procedure twice more or until the filtrate is clear. Then pour one 500 ml portion of distilled water into the jar and drain. The filtrate should be reasonably clear. Save all filtrate.

The purpose of the dispersing solution is to increase the pH and provide an environment of maximum dispersion.

FINES DETERMINATION

Wash the long fiber fraction left on the screen in the previous section onto a weighed filter paper and dry it. Calculate the percent fines as follows:

$$\text{Percent fines} = \frac{\text{Total solids weight} - \text{Long fiber weight} \times 100}{\text{Total solids weight}} \quad (7)$$

For this particular pulp formulation the fines percent was 26%.

FILLER TO CELLULOSE FINES RATIO

Ash the filtrate obtained during wet screening and determine its ash content. The filter to fines ratio is calculated as follows:

$$\text{Filler/fines ratio} = \frac{\text{Weight ash} \times \text{Filler factor}}{\text{Weight fines}} \quad (8)$$

For this particular experiment the filler/fines ratio was 2.25. This corresponded to a filler percentage of 18% and a cellulose fines percentage of 8%. The cellulose fines is simply the difference between the total fines content determined by wet screening and the filler percentage.

PREPARATION OF CHEMICALS

The following are the calculations of desired chemical concentrations to achieve the desired addition levels.

Assuming 500 ml of stock in the jar @ 0.5% consistency

$$500 \text{ ml} \times .005 = 2.5 \text{ grams of stock} \times \frac{1 \text{ lbs}}{453.6 \text{ grams}} = 5.51 \times 10^{-3} \text{ lbs of O.D fiber.}$$

For .75 lbs/ton Add-on-Level

$$\frac{5.51 \times 10^{-3} \text{ lbs}}{X} = \frac{2000 \text{ lbs}}{.75 \text{ lbs}} \times = 2.07 \times 10^{-6} \text{ lbs. of chemical}$$

$$2.07 \times 10^{-6} \text{ lbs} \times \frac{453.6 \text{ grams}}{1 \text{ lb.}} = 9.38 \times 10^{-4} \text{ grams of chemical}$$

Since 1.5 lbs/ton is twice 0.75 lbs/ton:

$$9.38 \times 10^{-4} \text{ grams} \times 2 = 1.876 \times 10^{-3} \text{ grams of chemical for 1.5 lbs/ton}$$

Two syringe sizes are available. A 10 ml syringe will be used to add 0.75 lbs/ton and a 20 ml syringe will be used to add 1.5 lbs/ton.

In order to minimize error due to measurement with the respective syringes, the solutions were made up in very dilute form, in 500 ml portions.

$$\frac{9.38 \times 10^{-4} \text{ grams}}{10 \text{ ml}} = \frac{X_1 \text{ grams}}{500 \text{ ml}} \quad \frac{1.876 \times 10^{-3} \text{ grams}}{20 \text{ ml}} = \frac{X_2 \text{ grams}}{500 \text{ ml}}$$

$X_1 = X_2 = 4.69 \times 10^{-2}$ grams diluted to 500 ml. This allows all solutions to be made up at the same concentration (9.38×10^{-3} g/ml).

RETENTION DETERMINATION

Take approximately 500 ml out of the master batch and record its weight. Admit the air pressure (6 oz/in^2) to the bottom of the jar and pour in the sample. Determine the amount of each chemical required by a simple ratio of the actual percent consistency to 0.5% consistency (the base figure used in the previous calculations) and

multiplying by the number of milliliters required for that addition level (10 ml for 0.75 lbs/ton and 20 ml for 1.5 lbs/ton). Set the stirrer to 300 rpm and allow it to run for 10 seconds. Add the first chemical (in this experiment the bridging agent was always added first). Wait 10 seconds and add the second chemical. After 30 seconds turn the agitator up to the desired speed. If no chemical is added, still wait 30 seconds before turning the speed up. After 50 seconds drain a 100 ml sample into a 100 ml beaker of accurately known weight. Weigh the sample plus beaker and record this weight. Filter the sample through a previously dried and weighed Watman #40 or comparable filter paper. Dry the filter paper plus filtrate residue in a fast drying circulating oven and determine its weight. It was found that placing the filter paper in a light, airtight plastic container while the paper was still in the oven and then weighing the container plus the paper resulted in greater accuracy on the filter paper and residue weights.

RETENTION CALCULATIONS

$$\text{Total solids (Ts)} = \text{Total grams of sample} \times \frac{\% \text{ solids}}{100} \quad (9)$$

$$\text{Total fines (T}_f\text{)} = \text{Ts} \times \frac{\% \text{ Fines fraction}}{100} \quad (10)$$

$$\text{Fines free in liquid phase (F}_1\text{)} = \text{Grams of fines aliquot} \times \frac{\text{Starting Sample weight}}{100} \quad (11)$$

$$\% \text{ Fines retention} = 100 - \frac{F_1}{T_f} \quad (100) \quad (12)$$

APPENDIX II

ACTUAL EXPERIMENTAL AND CALCULATED VALUES

EXPERIMENTAL DESIGN

600 rpm							1500 rpm					
	LRA			HRA			LRA			HRA		
	0	0.75	1.5	0	0.75	1.5	0	0.75	1.5	0	0.75	1.5
LBA												
0	001	002	003	004	005	006	007	008	009	010	011	012
	013	014	015	016	017	018	019	020	021	022	023	024
	025	026	027	028	029	030	031	032	033	034	035	036
0.75	037	038	039	040	041	042	043	044	045	046	047	048
	049	050	051	052	053	054	055	056	057	058	059	060
	061	062	063	064	065	066	067	068	069	070	071	072
1.5	073	074	075	076	077	078	079	080	081	082	083	084
	085	086	087	088	089	090	091	092	093	094	095	096
	097	098	099	100	101	102	103	104	105	106	107	108
HBA												
0	109	110	111	112	113	114	115	116	117	118	119	120
	121	122	123	124	125	126	127	128	129	130	131	132
	133	134	135	136	137	138	139	140	141	142	143	144
0.75	145	146	147	148	149	150	151	152	153	154	155	156
	157	158	159	160	161	162	163	164	165	166	167	168
	169	170	171	172	173	174	175	176	177	178	179	180
1.5	181	182	183	184	185	186	187	188	189	190	191	192
	193	194	195	196	197	198	199	200	201	202	203	204
	205	206	207	208	209	210	211	212	213	214	215	216

TABLE IB
ACTUAL EXPERIMENTAL RESULTS*

	600 rpm						1500 rpm					
	LRA			HRA			LRA			HRA		
	0	0.75	1.5	0	0.75	1.5	0	0.75	1.5	0	0.75	1.5
LBA												
0	10.4	35.3	(29.8)	(16.4)	34.0	45.9	9.0	25.1	16.3	6.2	17.7	12.1
	11.1	32.9	59.7	10.4	21.4	48.4	2.6	20.2	16.3	(19.1)	16.9	21.9
	11.3	36.1	61.9	(19.0)	(15.5)	41.2	11.5	24.7	14.7	(1.8)	17.8	(4.4)
0.75	20.6	30.1	43.4	23.6	42.2	50.2	9.9	13.9	14.3	16.4	18.3	25.5
	19.5	25.3	(77.7)	16.7	15.6	23.3	3.0	25.4	21.4	5.7	20.4	11.5
	22.9	37.1	53.4	24.8	32.6	26.0	(1.8)	5.8	18.9	(2.6)	16.1	9.2
1.5	18.1	66.6	50.3	10.1	39.5	(34.4)	4.6	21.2	30.0	16.5	21.6	9.8
	8.5	52.7	39.3	20.0	35.3	64.7	10.1	13.5	25.6	12.8	(6.9)	8.5
	4.3	61.7	42.4	7.4	53.0	64.9	9.45	11.4	20.1	20.8	23.2	(26.3)
HBA												
0	12.8	(26.2)	37.0	8.9	(15.4)	61.3	(12.9)	21.1	14.8	5.9	4.2	7.8
	9.2	33.3	31.9	(23.1)	30.7	(30.3)	10.8	11.2	13.3	(1.7)	23.1	21.1
	11.0	(59.1)	(79.5)	(16.5)	23.2	58.8	4.6	9.7	12.6	10.5	14.4	17.2
0.75	14.4	57.3	47.0	7.6	20.4	27.9	(21.4)	21.4	(18.2)	14.5	24.3	21.3
	23.2	61.3	49.2	25.5	(36.2)	30.1	13.6	22.3	33.7	11.7	18.7	24.2
	13.6	(26.7)	(82.8)	15.8	20.0	25.8	13.7	20.5	30.9	(3.9)	(6.9)	15.2
1.5	(6.5)	35.4	37.9	15.7	51.6	44.7	17.6	27.2	15.8	(1.4)	11.7	14.1
	20.0	47.3	49.7	19.4	31.3	59.8	13.4	21.3	16.3	5.0	16.6	11.5
	14.4	48.9	44.7	12.8	39.7	70.1	10.9	23.7	(28.9)	16.8	23.9	19.6

*Expressed as percentage

() value was discarded on basis of Q test.

TABLE IIA
AVERAGED EXPERIMENTAL VALUES*

	600 rpm						1500 rpm					
	LRA			HRA			LRA			HRA		
	0	0.75	1.5	0	0.75	1.5	0	0.75	1.5	0	0.75	1.5
LBA												
0	10.6	34.4	47.6	10.6	27.3	51.1	7.6	18.7	14.7	7.6	19.4	14.6
0.75	21.4	30.8	48.4	21.4	30.1	33.2	8.9	15.0	18.2	8.9	18.3	15.4
1.5	11.4	60.3	44.0	11.4	42.6	64.8	12.4	15.4	25.2	12.4	22.4	9.2
HBA												
0	10.6	34.4	47.6	10.6	27.3	51.1	7.6	18.7	14.7	7.6	19.4	14.6
0.75	16.7	59.3	48.1	16.7	20.2	27.9	13.4	21.4	32.3	13.4	21.5	20.2
1.5	16.5	43.9	44.1	16.5	40.9	58.2	12.7	24.1	16.0	12.7	17.4	15.1

* Expressed as percentage.

TABLE IIIA

PERCENT RETENTION REDUCTION DUE TO INCREASED SHEAR

	LRA			HRA		
	0	0.75	1.5	0	0.75	1.5
LBA						
0	28.3%	45.6%	69.1%	28.3%	28.9%	71.4%
0.75	58.4%	51.3%	62.4%	58.4%	39.2%	53.6%
1.5	(8.8%)*	74.5%	42.7%	(8.8%)*	47.4%	85.8%
HBA						
0	28.3%	45.6%	69.1%	28.3%	28.9%	71.4%
0.75	19.8%	63.9%	32.8%	19.8%	(6.4%)*	27.6%
1.5	23.0%	45.1%	63.7%	23.0%	57.4%	74.0%

*An increase in retention with increasing shear.

TABLE IVA
PERCENT RETENTION REDUCTION DUE TO INCREASING SHEAR

<u>LRA</u>	<u>LBA</u>	<u>%Ret</u>	<u>LRA</u>	<u>HBA</u>	<u>%Ret</u>	<u>HRA</u>	<u>LBA</u>	<u>%Ret</u>	<u>HRA</u>	<u>HBA</u>	<u>%Ret</u>
Total Level of Addition 0.75 lbs/ton											
0	0	28.3	0	0	28.3	0	0	28.2	0	0	28.3
0	0.75	58.4	0	0.75	19.8	0	0.75	58.4	0	0.75	19.8
0.75	0	45.6	0.75	0	45.6	0.75	0	28.9	0.75	0	28.9
Total Level of Addition 1.5 lbs/ton											
0	1.5	(8.8)*	0	1.5	23.0	0	1.5	(8.8)*	0	1.5	23.0
1.5	0	69.1	1.5	0	69.1	1.5	0	71.4	1.5	0	71.4
0.75	0.75	51.3	0.75	0.75	63.9	0.75	0.75	39.4	0.75	0.75	(6.4)*
Total Level of Addition 2.25 lbs/ton											
0.75	1.5	74.5	0.75	1.5	45.1	0.75	1.5	47.4	0.75	1.5	57.4
1.5	0.75	62.4	1.5	0.75	32.8	1.5	0.75	53.6	1.5	0.75	27.6
Total Level of Addition 3.00 lbs/ton											
1.5	1.5	42.7	1.5	1.5	63.7	1.5	1.5	85.8	1.5	1.5	74.0

* An actual increase in retention with increasing shear.

TABLE VA
PERCENT IMPROVEMENT IN RETENTION 1500 rpm

	LRA			HRA		
	0	0.75	1.5	0	0.75	1.5
LBA						
0	0%	146%	93%	0%	155%	92%
0.75	17%	97%	139%	17%	141%	103%
1.5	63%	103%	232%	63%	194%	21%
HBA						
0	0%	146%	93%	0%	155%	92%
0.75	76%	182%	325%	76%	183%	166%
1.5	67%	217%	110%	67%	129%	99%

* Based on the 0.0 level of addition retention of 7.6%.

TABLE VIA
PERCENT IMPROVEMENT IN RETENTION* 600 rpm

	LRA			HRA		
	<u>0</u>	<u>0.75</u>	<u>1.5</u>	<u>0</u>	<u>0.75</u>	<u>1.5</u>
LBA						
0	0%	224%	349%	0%	158%	382%
0.75	102%	190%	356%	102%	184%	213%
1.5	8%	469%	315%	8%	302%	511%
HBA						
0	0%	224%	349%	0%	158%	382%
0.75	58%	459%	354%	58%	91%	163%
1.5	57%	314%	316%	57%	286%	449%

* Based on the 0.0 level of addition retention of 10.6%.