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The Repulpability of Coated Broke Containing Latexes and Its Effects on a Rosin - Alum Sizing System

by
Walter Cordell III

A Thesis Submitted
in Partial Fulfillment of
The Course Requirements for
The Bachelor of Science Degree

Western Michigan University
Kalamazoo, Michigan

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ABSTRACT

It is the purpose of this thesis to attempt to evaluate the repulpability of coated papers that contain latex as a binder, and also to evaluate the effects of an alum-rosin sizing system on the latex particles, as well as any bundles of fibers or fibers and coating.

It has been found that SBR latex will break up with the greatest difficulty, probably due to its added stability imparted by the carboxyl group attached to it. The PVAC and acrylic latexes break up much easier than the SBR under the same conditions, with the acrylic breaking up more readily than the PVAC. This trend is evident at all addition levels of the latexes from 100% down to 25%.

The alum-rosin sizing system does have an effect on the latexes, generally causing from one to two and a half times the build up on the dynamic screen than did the 100% starch sample under the same conditions. The amount of buildup is a function of particle size. The bigger the particle, the larger the amount of buildup. This effect is more pronounced at higher levels of addition, but is evident at all levels of latex. The rosin-alum sizing system has a larger effect on coated papers with latex as a binder than on coated papers containing starch as the only adhesive.

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The Repulpability of Coated Broke Containing Latexes and Its Effects On A Rosin Alum Sizing System

Introduction

The problem of broke recovery of latex coated paper stocks has been with the paper industry since the first latexes were used.(13) The difficulty in broke recovery systems is that the different latexes respond to different treatments to facilitate broke recovery.(13) Some are hydrophilic, some are hydrophobic; still others respond to alkaline treatments and others to acid treatments.(17) In this paper an attempt will be made to determine what variables are most important to effectively repulp coated broke so that it will not interfere with other parts of the papermaking process, such as formation on the wire, where alum and rosin are likely to be introduced.

Styrene butadiene, polyvinyl acetate, and acrylic latexes will be studied in this paper. A 100% clay coating will be formulated containing varying amounts of starch and latex. A base stock of 32#/ream (25 x 38 - 500) containing high groundwood content will be coated on one side at 6 lbs $\pm$ .5 lb. per same ream size. The high groundwood content base stock was chosen because it will be easily broken up on repulping, and also to allow good coating penetration. The paper will be repulped in a waring blender, using a standard charge of 400 grams, at 4% consistency varying time, temperature, and pH. After repulping, a sample will be removed, diluted to .5% consistency, and first screened in a jar under dynamic condition using the same pH and temperature conditions. Reject percentages will be determined quantitatively by weighing the screens before and after each use. Similar samples will

then be screened in a jar, introducing alum and rosin into the system, and determining the rejects quantitatively. Any observed differences in percent rejects will hopefully leave an opportunity for possible speculation of flocculation and build-up mechanisms related to the above described system, as they might relate to paper machine conditions, to some degree. A sample will also be screened using a large mesh, to catch the large debris that is not caught in the dynamic jar.

Literature Survey

Historical Introduction

The use of pigmented coatings containing synthetic latexes was first introduced in the middle 1920's, and was used for "elegant" and expensive grades of paper.(3,22) This method incorporated the use of rubber latex and shellac to replace casein as the adhesive in paper coatings.(3) The General Rubber Company was issued a patent in 1930 for this process. The Naugatuck Chemical Company first recognized the problem of oxidation of rubber and was issued a patent in 1934 for the use of triethanolamine as a softener.(3,8) Some commercial production of synthetic latexes started during the early 1930's. These first products were typically polycholoroprene and several esters of polyacrylic acid. These were not in frequent use because of their high price.

The first significant breakthrough in the use of latexes occurred in 1946, in time to begin catching up with advances made in printing technology.(1) In 1946, the first commercial use of an SBR copolymer came into existance.(1,4) This latex was available at an affordable price. In 1948 it was discovered that latex could be crosslinked with starch to waterproof the system for offset, when modified water resistance was all that was needed. (3) Since this time, many advances have been made to improve the SBR copolymer, and the synthetic latex industry has been discovering new, improved products as well.(17,4)

Repulping of broke in the form of imperfect hand made sheets has been practiced since as early as 1795, but with the advent of bigger, faster

machines, and the increased usage of chemical additives, the real economics of the process has been recognized.(14) Any type of recycled fibers, be they wastepaper or clean mill broke is considered "secondary fiber". Pulp cost is the greatest single factor inducing mills to consider the use of secondary fiber.(7,14) Latex particles are insoluble and can be detrimental to the quality of repulped broke, as they prevent complete disintegration of the clay coating, resulting in course colored particles in the pulp.(13,14)

Sizing of paper with rosin is one of the oldest chemical processes in papermaking.(23) Sizing, since its discovery in 1804, has developed into an art. Because of the complexity of the mechanism, and the large number of variables associated with it, a simple, valid theory has not yet been developed. The advantages and uses of the alum-rosin sizing system has been under research for years.(24) Its behavior under certain conditions has been studied, and the key parameters to its success are uniform distribution and orientation of the size.(23)

Theoretical Discussion

Factors Affecting Synthetic Binder Performance

Polymer Stability: Polymer stability is the most basic and important characteristic property a latex posesses.(15) Polymer stability can be defined as its ability to maintain its distinctive particle characteristic without coagulating.(20) This particle characteristic is affected by several variables in the papermaking process: shear rates, metallic ions, temperature, pH, pigments, defoamers, and other binders. Since most latexes are used in conjunction with other adhesives, their compatability is very important. Stability is a function of three latex variables.(15):

1) Particle size - The larger particle size latex is more stable since its total polymer surface area is less and therefore more emulsifier molecules are available to stabilize each particle. However, a smaller particle size gives better binding strength. The smaller particles act like tiny spot welds to hold the coating to the fibers.

2) Particle Composition - Generally, the harder the latex sphere, the greater the stability the system has.

3) Emulsifier Type - The sphere is coated with an emulsifier. These are usually anionic or nonionic and enhance stability.

Monomer Type: The type of monomer selected or the ratio selected has a strong influence on basic polymer properties.(1) Selecting a hard monomer to soft monomer ratio of styrene to butadiene, with a much higher percentage of styrene, results in a latex with good binding capabilities. The affinity of the monomer to compounds other than another monomer also has an affect on the polymer stability.(1,12)

Film Formation: Formation of a good film provides toughness, adhesion,

and durability.(15,16) Film formation begins when sufficient water is lost from the coating, and pigment and binder particles begin to pack together.(1) The latex particles distort, which brings them into closer contact. The driving force behind film formation is the capillary action of the water present; the opposing force is the resistance to deformation of the particles. (1,16).

Glass Transition Temperature: The glass transition temperature of the polymer also affects film formation, as the polymer remains flexable above Tg, allowing for better film formation, due to the localized mobility of the polymer above Tg.(20) Throughout the entire coating process, the temperature must remain above Tg, as this allows the particles to pack closely together. (16) Although Tg is useful in characterizing a polymer, it should not be used solely to rate the efficiency of polymer binders, as many other factors, such as copolymerizable acid content, molecular weight, and particle size do exert an influence on the film formation.(1)

Chemistry of Latexes

Definition of a Latex: A latex may be defined as a synthetic resin emulsion made of a dispersion of very small water insoluble particles held in aqueous suspension by a balance of surface active agents.(1)

Chemical Description and Physical Properties

Styrene Butadiene. This latex is a copolymer of at least two monomers; styrene and butadiene in water suspension.(1,8) In the case of the styrene butadiene presented in this paper, it is a carboxylated styrene butadiene,

which means a carboxyl group has been added to the molecule for added stability. (12) The physical properties and stability of this latex are controlled for the most part by the ratio of styrene to butadiene in the final polymer. Styrene by itself is a hard, thermoplastic polymer. Butadiene, on the other hand, is a soft, flexable, elastic polymer.(1)

TABLE I (1,8) Structural Formulas of Latex Monomer Units

Butadiene	$H_2C = CH - CH_2$
Styrene	 $- CH = CH_2$
Vinyl Acetate	$CH_2 = CH - O - \underset{\underset{O}{\|}}{C} - CH_3$
Acrylic (monomers are derivatives of acrylic acid)	$CH_2 = CHCOOH$

<u>Polyvinyl Acetate:</u> Vinyl acetate monomer is polymerized readily in emulsion form by itself. The water purity is essential for uniformity. The flexability is varied through copolymerization with a variety of vinyl monomers. Stabilization is controlled by reaction rate, temperature, co-monomers, and selection of surfactant. Physical properties include softness, resistance to ink attack, and improved ink transfer.(1,10).

<u>Acrylic Latex:</u> All acrylic polymers are made from monomers of synthetic resins based on esters of acrylic and methacrylic acid. Monomers of the acrylic family are easily copolymerized with each other and other monomers. Polymers of low acrylic esters are soft, of middle acrylic esters are tacky,

and of high acrylic esters are waxy.(1) Three or more of these monomers are usually polymerized.(8) These polymers offer excellent shear stability, low odor, and resistance to yellowing. They also offer outstanding resistance to light, heat, and chemical degredation.(1,11)

Suggested Coating Formulations

There is no set coating formulation for each grade of paper to be produced, as factors such as basis weight of base stock, type of base stock, coating method, etc., each influences the coating. Coating method is important in determining certain physical characteristics of the coating, such as percent solids and viscosity. The formulations in the following tables are suggested starting points and may need to be modified according to each mill's needs.(1)

TABLE II (1) General Rule of Thumb of Binder Levels

Printing Method	Total Binder Level Per 100 Parts Pigment (Solids on Solids)
sheet offset	14-20
web offset	12-18
sheet letterpress	8-16
web letterpress	10-16
rotogravure	7-12

TABLE III (1) Typical SBR Formulations		
These components common to all grades listed	Pigment	100 Parts
	Dispersants	As Needed
	Antifoamer, etc.	As Needed
GRADE: Premium Enamel (sheet offset), size press 40% solids, 15.0 lbs/ream (25 x 38 - 500)/side		
	Protein	5 parts
	Latex	15 parts
GRADE: No. 1 Enamel (sheet offset), blade topcoat 60-65% solids, 6-9 lbs/ream (25 x 38 - 500)/side		
	Protein	4-6 parts
	Latex	10-12 parts
GRADE: No. 3 Enamel (sheet offset), blade 60-65% solids, 6-9 lbs/ream (25 x 38 - 500)/side		
	Starch	4-10 parts
	Latex	8-14 parts

TABLE IV (1) Typical Acrylic Latex Coating Formulations		
These components common to all grades listed	Pigment	100 Parts
	Dispersant	As Needed
	Defoamer	As Needed
For Web Offset, Trailing Blade 60-65% solids		
	Starch	10 parts
	Latex	5 parts
For Letterpress, Trailing blade 60-65% solids		
	Starch	14 parts
	Latex	2 parts
For Rotogravure, Air Knife 40% solids		
	Starch	As Needed
	Latex	6-10 parts

Presently, coating formulations for polyvinyl acetate need to be determined in the lab.(1) As a general rule, latex is always added last after the jet cooker and any additional high shear equipment.(1,9,15)

Types of Polymerization

Bulk: In this process the monomers are all added to the reaction vessel, a catalyst is added, and the reaction proceeds.(1,20)

Solution: The monomers are first put into solution, catalyst is added, and the reaction proceeds.(1,20)

Suspension: During the reaction, large particles are suspended.(20)

Emulsion: This is the process which concerns the latexes discussed in this paper, and will be discussed in greater detail.

Monomers are suspended as droplets in a water phase by means of an emulsifying agent.(16) Polymerization is initiated by free radicals formed by thermal decomposition of a peroxy compound.(19) Polymerization is controlled by the number of free radicals present, emulsifier concentration, monomer concentration, and temperature.(1,20)

At the beginning of the reaction there are three distinct phases which monomers are present in:

1) Large monomer droplets.
2) In monomer swollen emulsifier micelles.
3) Dissolved in water phase.

Initiation occurs in micelles and aqueous stage because of large surface area present. The particle size is determined in the first stages of the reaction. Extensive crosslinking should be avoided since it reduces desired coating properties.(1,15)

Factors Affecting Repulpability of Broke

Temperature: The optimum temperature is 160°F. However, latexes are best removed from the system at temperatures below their Tg.(7)

Time: Varies with stock to be broked, pH, consistency and temperature.

pH: The best pH for repulping printing broke is on the alkaline side, since most inks are alkaline soluble.(5) However, latexes are alkali sensitive, and would coagulate at low pH, which might make them easier to remove from the system.

Consistency: Optimum repulping consistency should be 4 to 5 percent. Fiber to fiber, particle to fiber, and particle to particle disintegration is dependent upon consistency, but must be kept on this low end for various reasons, i.e. power consumption is too great at high consistencies.

Shear Forces: These forces are induced by impellors, and the direction is dependent upon the speed of the impellor, the impellor angle and the shape and design of the vessel.(14)

Wettability of the Substance: The wettability of a substance depends mainly upon any surface sizing materials. Once the surface has been "wetted", then the internal structure must also be wetted. The rate of diffusion of the water into the broke is not aided by agitation, but is related to the first four variables listed above.(5)

Factors Affecting Rosin-Alum Sizing Systems

Uniform Distribution of the Size: The smaller the particle size, the smaller the tendency to agglomerate, and the more efficient the size. This smaller particle size is achieved through fortification of the rosin sizes.(23)

Maleic anhydride has been known to fortify rosin sizes for the last 25 years. (24) The maleopimaric acid, which is mainly responsible for the fortification action, orients itself horizontally, rather than vertically as the rosin acids do, so that all carboxyl groups do, to a degree, become involved in the interaction with the aluminum ions.(23) Collection of this acid at the interface of the complex or micelle results in a strong negative charge, which induces enlargement of the surface area, which results in a smaller particle size. Residual alum or calcium from hard water cause premature agglomeration of rosin size and cause the loss in efficiency. These aggregates are quite unevenly distributed.(23,24)

<u>Orientation of the Size</u>: All of the factors listed above also are important to proper orientation of the size. The most important factor is probably the horizontal orientation of the maleopimaric acid, forcing all carboxyl groups to become involved in the interactions with aluminum ions. pH is very important to both distribution and orientation, a pH of 4.5 being best, below 3.5 no sizing occurs because of an inadequate amount of alumina present in the sheet. Alumina is important because it reverses the charge on the rosin and anchors the rosin into the fibers to promote orientation. The rosin carboxyl is either intramolecularly coordinated with one aluminum atom or forms a coordination bridge with 2, imposing a permanent preferential orientation of the rosin molecule.(23,24). Above pH 6, the size precipitate becomes isoelectric, and strong aggregation sets in which reduces sizing efficiency.

Experimental Procedure

Materials Used

Clay: predispersed, domestic, with a particle size of 82 percent less than 2 mu.

Starch: Penford Gum 280.

Paper: 32 lb (25 x 38 - 500), high groundwood content.

Latexes: As described in literature survey.

Chemicals: NaOH, HCl for pH control. Alum, Rosin stock solutions.

Equipment Used

Keegan Coater: lab scale, blade type.

Cowles dissolver: lab scale, for dispersing pigment.

Waring blender: quart size, for repulping vessel.

Dynamic Jar: with rotating screen and magnetic mixer, as described in appendix one.

Coating Preparation

The clay was prepared batch style as needed.

The clay was dispersed using a Cowles dissolver at 70% solids with .5% TSPP as dispersing agent. The clay was dispersed for 20 minutes.

The starch was prepared batch style as needed.

The starch was dispersed with a Cowles dissolver at 25% solids for 10 minutes. The starch was wetted first with cold water, then heated on a steam bath to 80-85^{o}C while shear was applied.

The starch was added to the clay after the clay was dispersed for the

full 20 minutes. The starch was mixed into the clay for an additional 10 minutes. The dissolver was then slowed down greatly, and the latex added at such a rate as to avoid foaming as much as possible. The latex was mixed in for 3 minutes.

A total of 13 coatings were prepared with a total adhesive level of 20 pph. This was divided as follows: 1 starch blank, 25%, 50%, 75%, and 100% latex for each of the three latexes.

Coating and Drying Procedure

The coating was applied at 55% solids using a lab scale Keegan coater to give a coat weight of 6 $\pm$ .5 lbs/side/ream (25 x 38 - 500). One side only was coated. The coater was run at 15 fpm. The coatings were dried at high temperatures using the heaters on the coater and an additional space heater right after the blade. The purpose of the high temperatures, especially for the SBR, was to aid in crosslinking the latexes. The dried sheets were then cured in an oven at 125^{o}F for at least 2 days, to enable the latexes to further crosslink.

Repulping Procedure

A one quart capacity waring blender was used as a repulping vessel. In case of a variable speed blender, the lowest speed was used. A total charge of 400g of coated paper at 4% consistency in distilled water was used as a standard charge. A sample of each of the thirteen coatings was repulped. The paper was cut into 1" square sizes. The squares were allowed to soak in the blender for 30 seconds prior to repulping. The three variables studied and their values are as follows:

time (sec)	temp (^{o}C)	pH
30	20	5
90	50	7
150	80	9

As one column is varied, the others will be kept at their mean values.

After repulping, the sample was diluted to 3200 ml at .5% consistency and screened as outlined in the following section.

Screening Procedure

Stationary Method: A 1200 ml sample of the diluted stock was poured into an 8-mesh screen, which is contained in a 10 inch diameter frame with 2 inch sides. It was washed under a laboratory faucet using a flow rate of 3 liters/min for 3 minutes. The screen was rotated during this time to wash through all the small fibers and bundles of fiber and coating. The screen was then dried and weighed, and the percent debris retained on the screen was recorded.

Dynamic Method: This method of screening operates as follows: Five 400 ml samples of the diluted stock were screened individually in the jar operating at a pH of 4.5 and a temperature of 20^{o}C. The samples were treated as follows:

Sample	Percent Rosin	Percent Alum
A	0	0
B	3	0
C	2	1
D	1	2
E	0	3

The rosin and alum percentages are based on fiber weight. The rosin and alum were prepared as stock solutions so 1 ml = 1% to avoid any excessive dilution of the samples.

The conditions of pH = 4.5 and temp = 20°C were established in the jar before any alum or rosin was added. The 10 mesh screen was lowered into a one liter beaker, and the sample was poured down the sides, not directly onto the screen. The beaker was positioned onto a magnetic mixer before the screen was lowered into it. The magnetic mixer and the screen both rotate in the same direction at different speeds. The screen rotates at 30 RPM, the mixing bar at 60 RPM, simultaneously for 1 minute total. The purpose of the mixing bar is to kick up the stock suspension to allow it to catch on the screen. The screens were removed and dried and the percent debris retained was recorded. See appendix one for a complete diagram.

Data and Results

It was expected from the beginning that each of the three latexes should break up in varying amounts under different repulping conditions of pH, temperature, and time. However, the amount of disintegration of each latex compared to the other two was not known. It was expected that the SBR would break up less than the other two, but it was not known how the PVAC and acrylic would compare to the SBR and to each other. One sample of each of the thirteen coated stocks was repulped and screened. At optimum conditions of pH, time, and temperature, the percentage of SBR retained on the 8 mesh screen at 100% addition levels is about 8%, compared to 30% at the worst conditions. This relative difference is maintained through all levels of addition, although the percentages drop. For 100% PVAC, optimum conditions equals about 3% retained, where worst conditions equals 13% retained. Again this relative difference is noticeable through all addition levels. For acrylic, optimum is 0% retained, while worst is about 5% retained. These percentages drop as the addition levels drop. The stationary method of screening gave a definite difference in the degree of repulpability of each of the stocks containing latexes. The dynamic method also gave results corresponding to the degree of repulpability, but not as clearly as the stationary method; however the results did come up 80% positive, leaving room for interpretation. This data is shown by exact figures in Appendix 2, and graphically on the following pages in figures 1-48.

The graphs are divided into groups as follows: In the first twelve figures, the stationary screening method was used, as described in the ex-

perimental procedure. In figures 1-4, the amounts of latex present as binder are varied from 100% in figure 1 to 25% in figure 4. The repulping times are varied on each graph, and the pH and temperature are constant at 7 and 50°C, respectively. In figures 5-8, the amounts of latex are again varied from 100% in figure 5 to 25% in figure 8. The repulping temperature is varied on each graph, with the pH = 7 and the time = 90 seconds. In figures 9-12, the amount of latex as binder is varied from 100% in figure 9 to 25% in figure 12. The repulping pH is varied on each graph, and the time and temperature is constant at 90 seconds and 50°C, respectively. In all cases the percent debris (dependent variable) is plotted against time, temperature, or pH (independent variable). On these first twelve graphs an attempt was made to keep the scales the same to make any trends easily recognizable, but this was not possible if clear, readable graphs were to be obtained. The graphs can be easily transposed if necessary.

In figures 13-48, the dynamic method of screening was implemented, as described in the experimental procedure. In figures 13-15, the repulping time is varied from 30 seconds in figure 13 to 150 seconds in figure 15. The pH and temperature is constant at 7 and 50°C, respectively. The paper repulped in these three graphs all contain 100% latex as binder. The percent debris is plotted against the percent alum and percent rosin, which are based on fiber weight. In figures 16-18, the conditions of repulping time, temperature and pH are the same as in figures 13-15. However, in figures 16-18, the latex level of addition is 75% of the total binding system. In figures 19-24, the same repulping conditions exist as in figures 13-15, except in figures 19-21 the latex level is 50%, and in figures 22-24 the latex level

is 25% of the total binding system. In figures 25-27, the repulping temperature is varied from 20°C in figure 25 to 80°C in figure 27. The pH and time and constant at 7 and 90 seconds, respectively. The paper repulped in these three graphs all contain 100% latex as binder. Again the percent debris is plotted against the percent alum and percent rosin. In figures 28-36, the same conditions exist as in figures 25-27, except figures 28-30 contain 75% latex, figures 31-33 contain 50% latex, and figures 34-36 contain 25% latex. In figures 37-39, the repulping pH is varied from 5 in figure 37 to 9 in figure 39. The time and temperature are 90 seconds and 50°C, respectively. The paper repulped in these graphs all contain 100% latex as binder. Both debris percentages and rosin-alum percentages are plotted against each other. In figures 40-48, the same conditions exist for each series of three graphs, except figures 40-42 contain 75% latex, figures 43-45 contain 50% latex, and figures 46-48 contain 25% latex.

Since it was not possible to plot the exact values on the graphs, the following system is used to identify the latexes.

Styrene butadiene (SBR)	—— △ —— △ ——
Acrylic emulsion (acrylic)	—— □ —— □ ——
Polyvinyl acetate (PVAC)	—— ○ —— ○ ——
Starch blank (starch)	—— * —— * ——

Figure 1: Coated paper containing 100% latex binder. Repulping time varied, pH=7, and temperature=50°C.

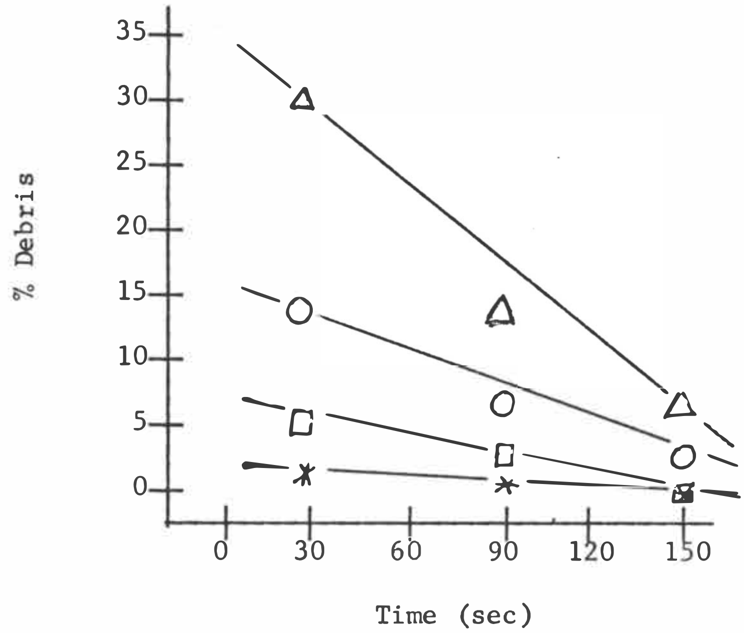


Figure 2: Coated paper containing 75% latex and 25% starch as binders. Repulping time varied, pH=7, and temperature=50°C.

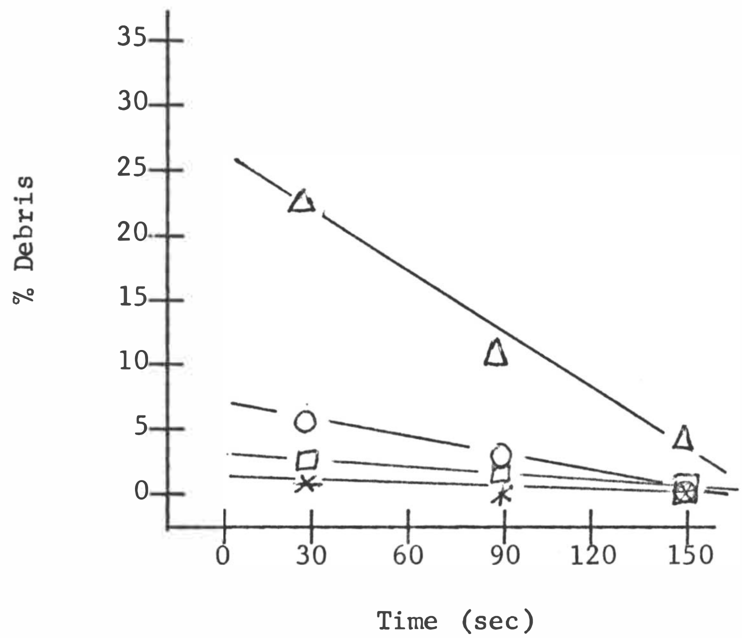


Figure 3: Coated paper containing 50% latex and 50% starch as binders. Repulping time varied, pH=7, and temperature=50^{o}C.

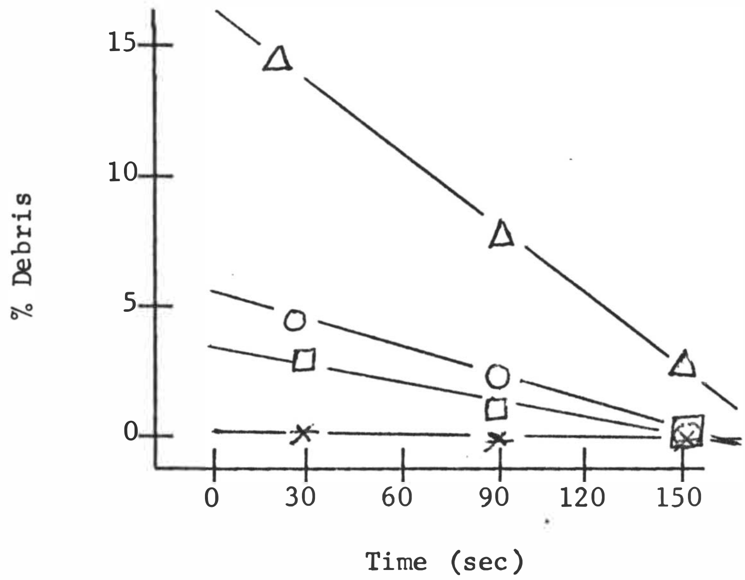


Figure 4: Coated paper containing 25% latex and 75% starch as binders. Repulping time varied, pH=7, and temperature=50^{o}C.

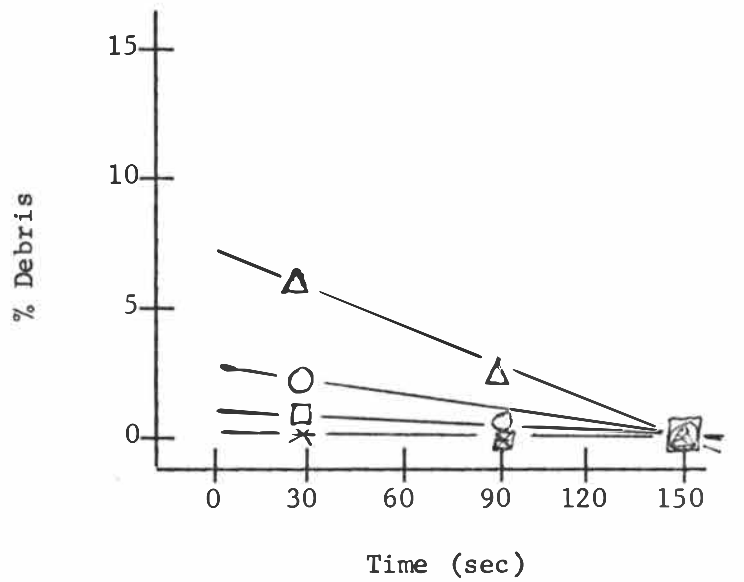


Figure 5: Coated paper containing 100% latex binder. Repulping temperature varied, pH=7, and time=90 sec.

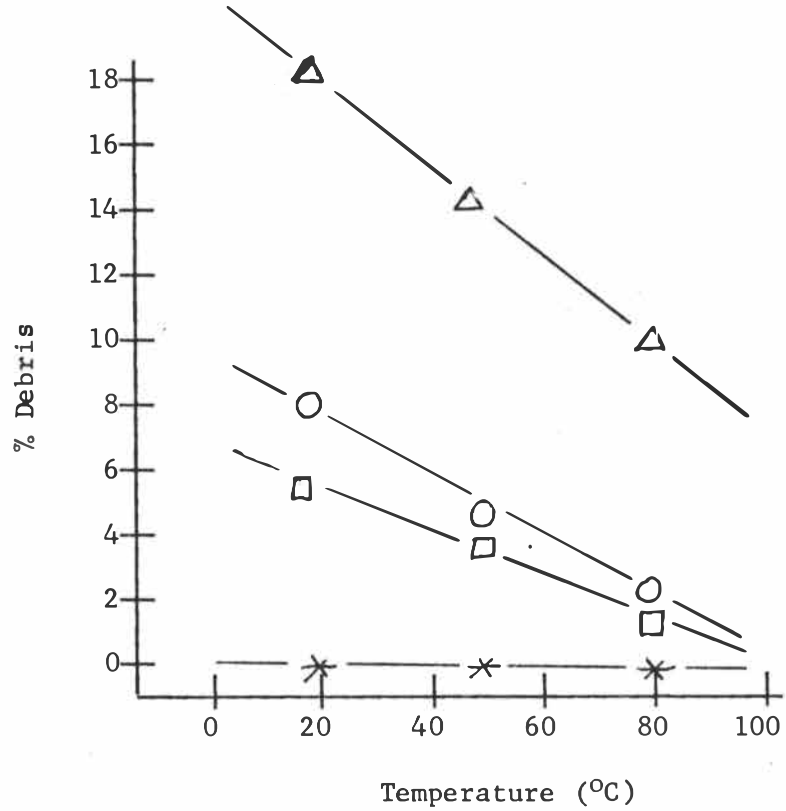


Figure 6: Coated paper containing 75% latex and 25% starch as binders. Repulping temperature varied, pH=7, and time=90 sec.

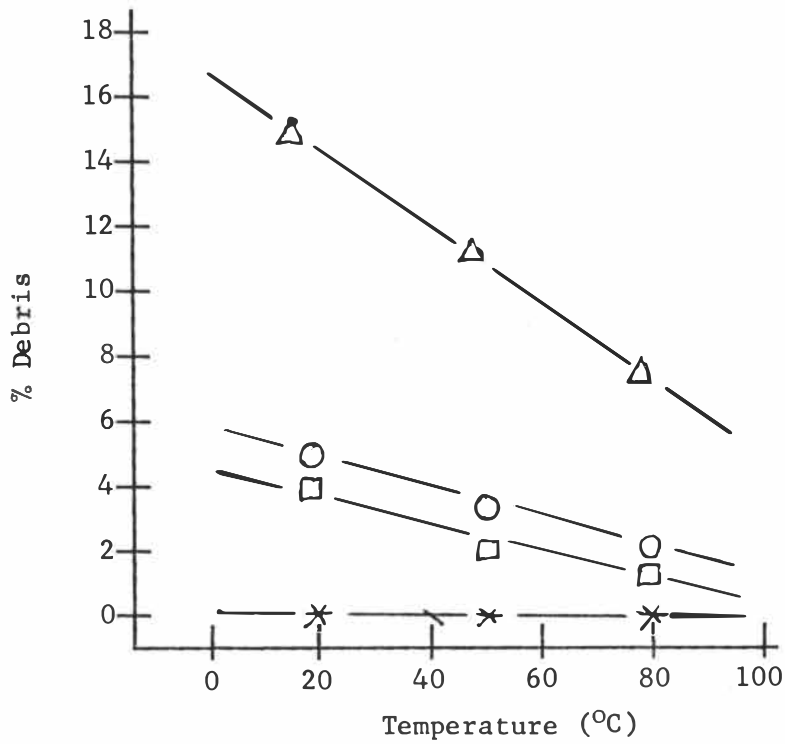


Figure 7: Coated paper containing 50% latex and 50% starch as binders. Repulping temperature varied, pH=7, and time=90 sec.

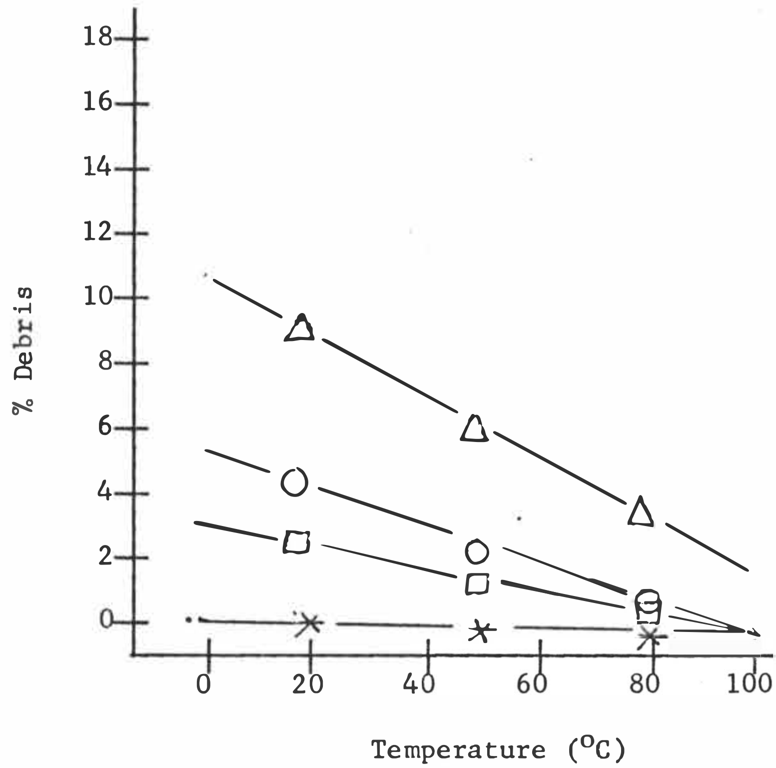


Figure 8: Coated paper containing 25% latex and 75% starch as binders. Repulping temperature varied, pH=7, and time=90 sec.

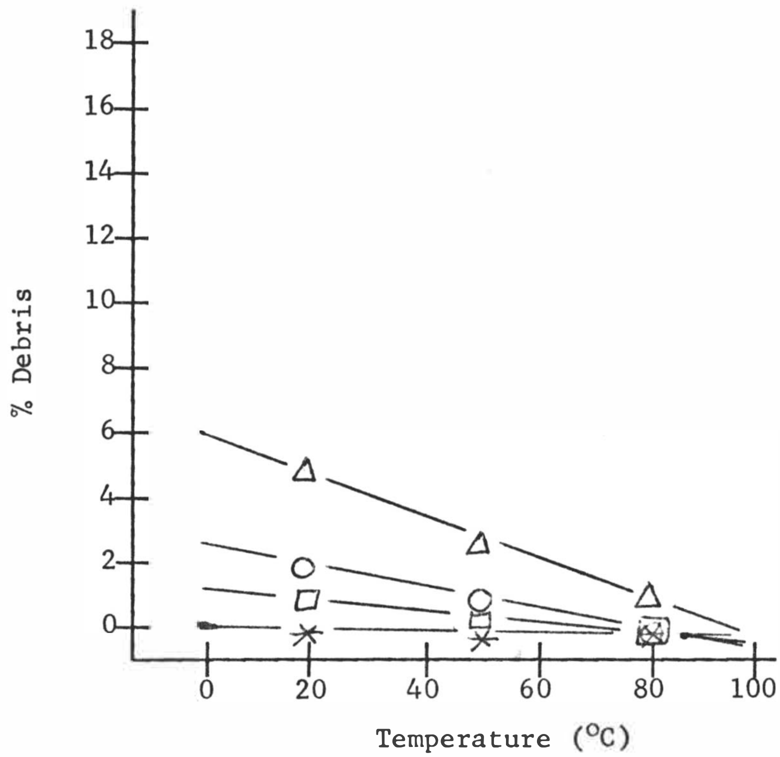


Figure 9: Coated paper containing 100% latex as binder. Repulping pH varied, time=90 sec, and temperature=50°C.

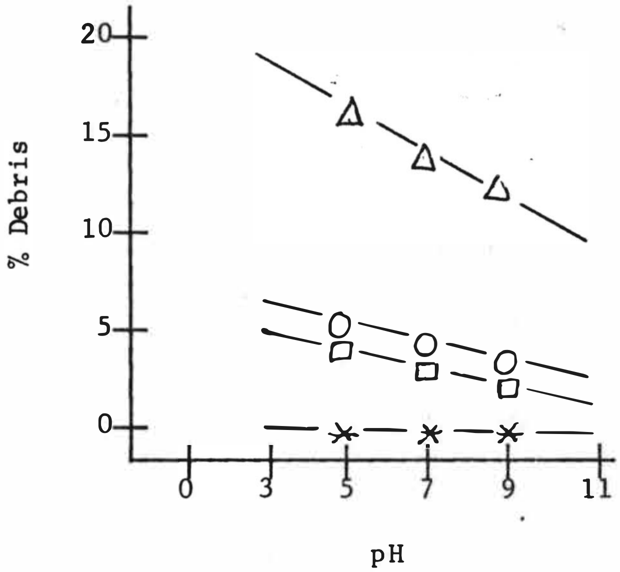


Figure 10: Coated paper containing 75% latex and 25% starch as binders. Repulping pH varied, time=90 sec, and temperature=50°C.

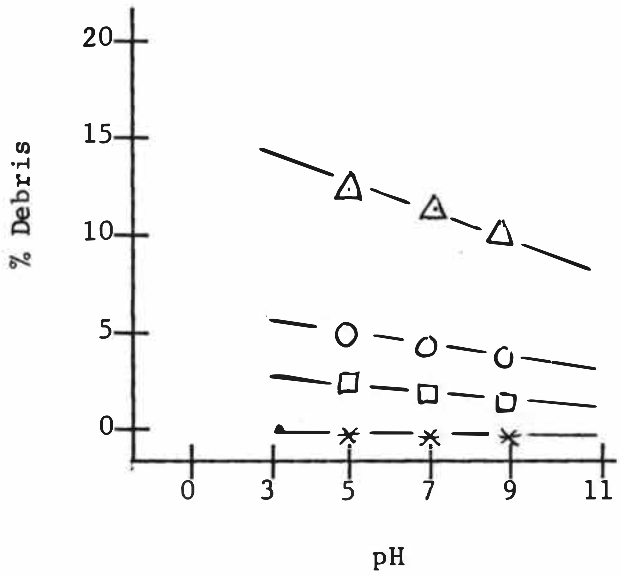


Figure 11: Coated paper containing 50% latex and 50% starch as binders. Repulping pH varied, time=90 sec, and temperature=50°C.

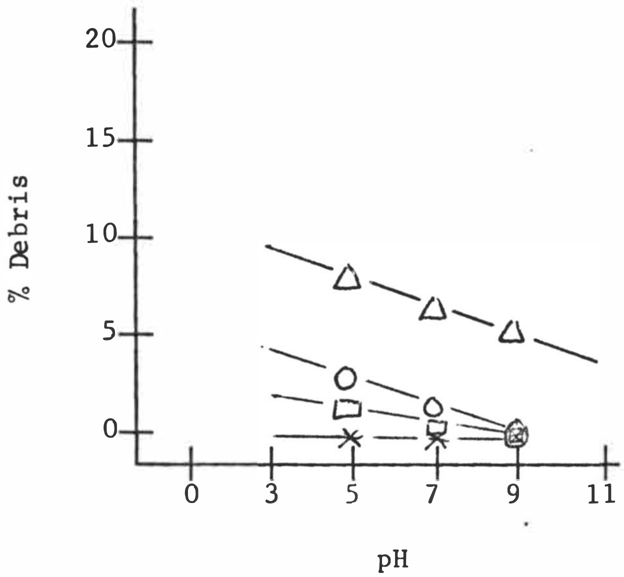


Figure 12: Coated paper containing 25% latex and 75% starch as binders. Repulping pH varied, time=90 sec, and temperature=50°C.

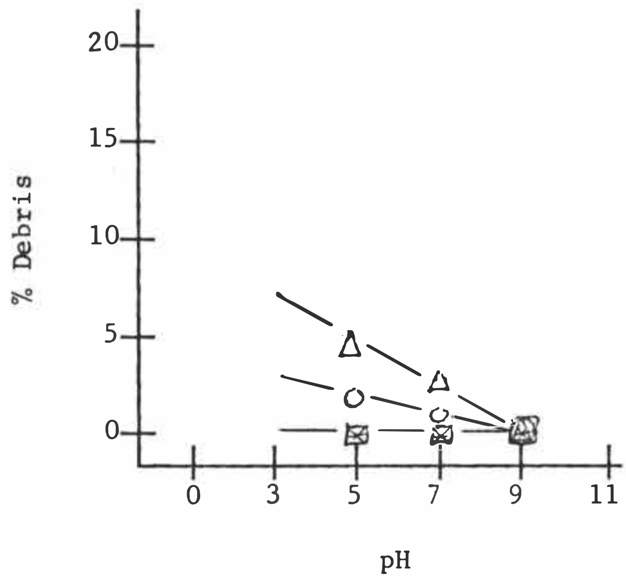


Figure 13: Coated paper containing 100% latex as binder. Repulping time=30 sec, pH=7, and temperature= 50°C.

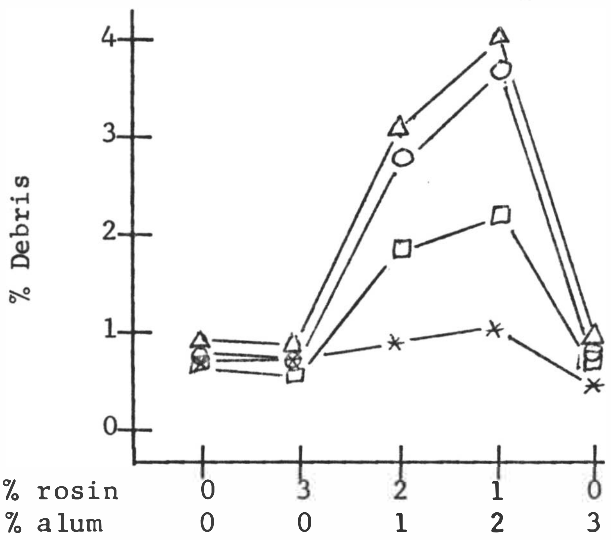


Figure 14: Coated paper containing 100% latex as binder. Repulping time=90 sec, pH=7, and temperature= 50°C.

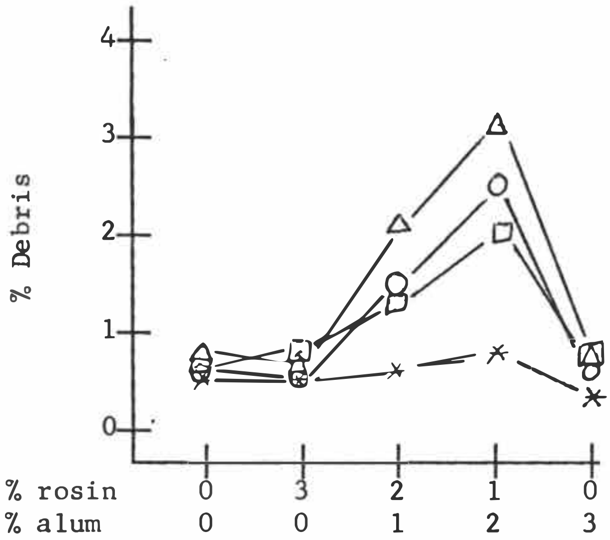


Figure 15: Coated paper containing 100% latex as binder. Repulping time=150 sec, pH=7, and temperature=50°C.

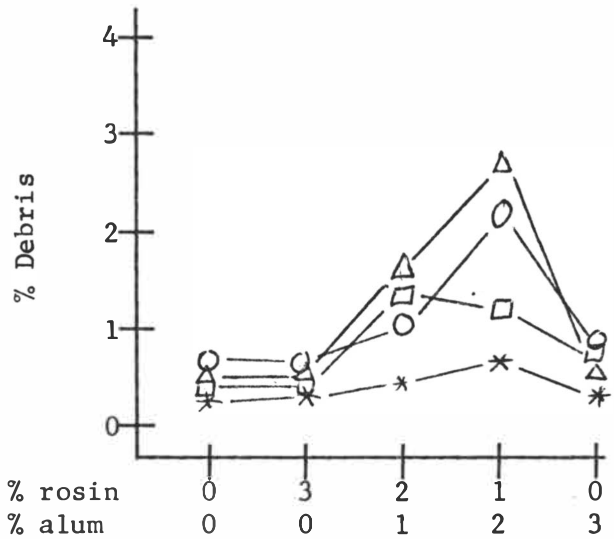


Figure 16: Coated paper containing 75% latex and 25% starch as binders. Repulping time=30 sec, pH=7, and temperature=50°C.

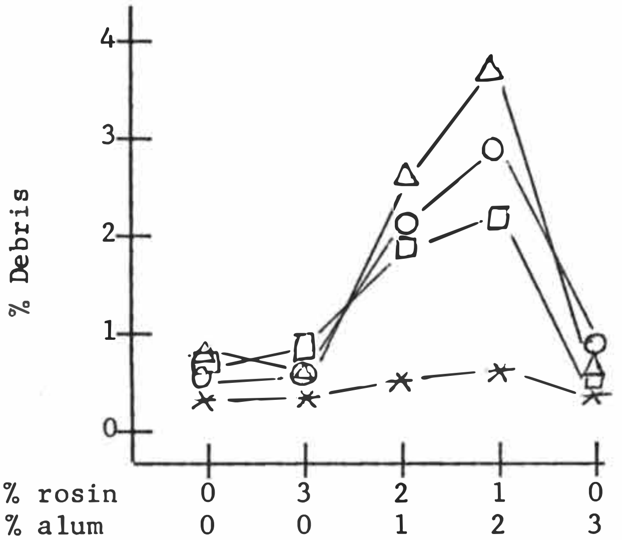


Figure 17: Coated paper containing 75% latex and 25% starch as binders. Repulping time=90 sec, pH=7, and temperature=50°C.

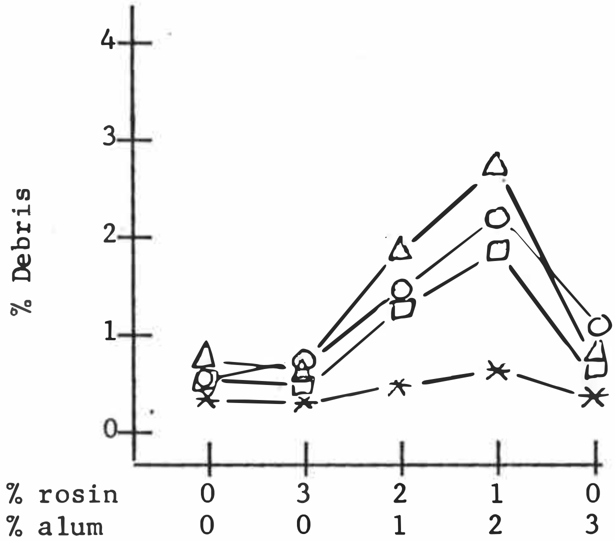


Figure 18: Coated paper containing 75% latex and 25% starch as binders. Repulping time=150 sec, pH=7, and temperature=50°C.

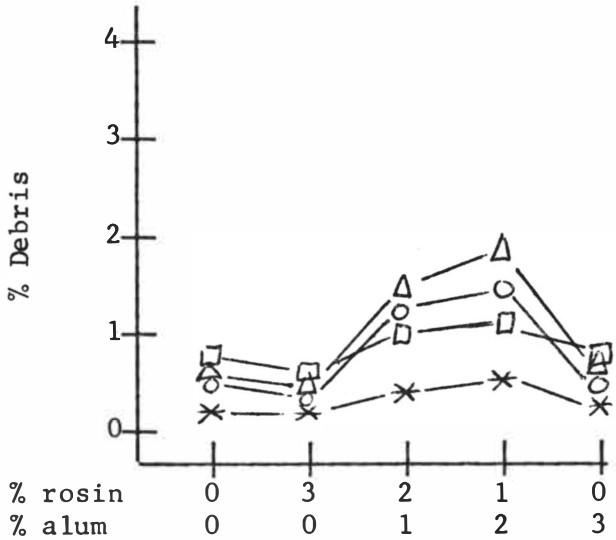


Figure 19: Coated paper containing 50% latex and 50% starch as binders. Repulping time=30 sec, pH=7, and temperature=50°C.

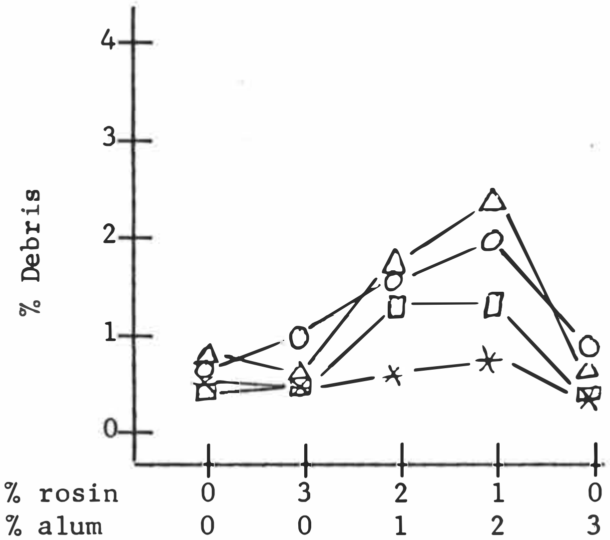


Figure 20: Coated paper containing 50% latex and 50% starch as binders. Repulping time=90 sec, pH=7, and temperature=50°C.

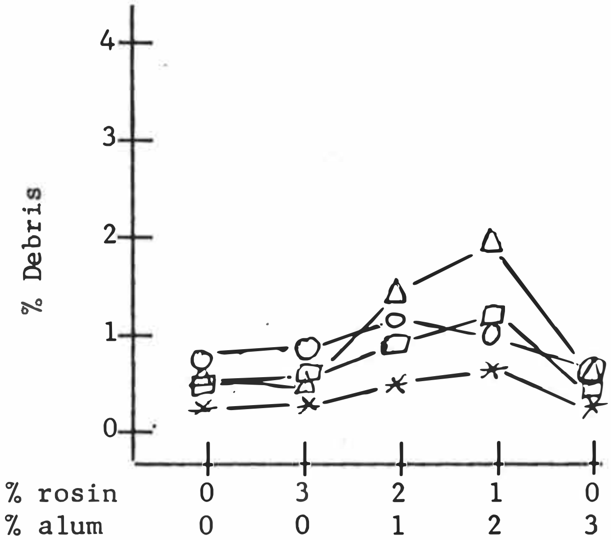


Figure 21: Coated paper containing 50% latex and 50% starch as binders. Repulping time=150 sec, pH=7, and temperature=50°C.

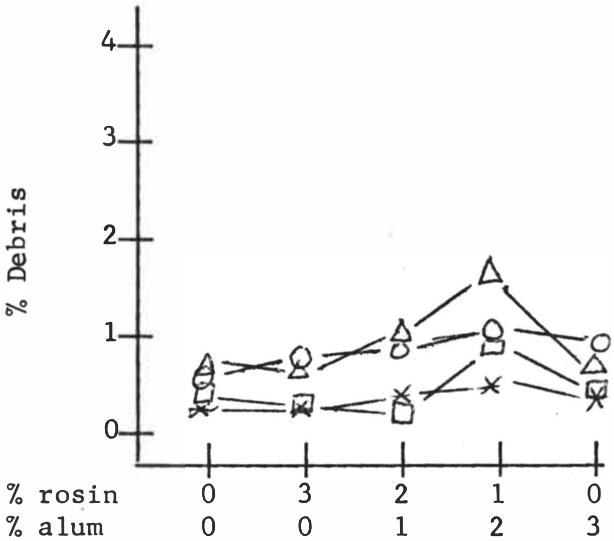


Figure 22: Coated paper containing 25% latex and 75% starch as binders. Repulping time=30 sec, pH=7, and temperature=50°C.

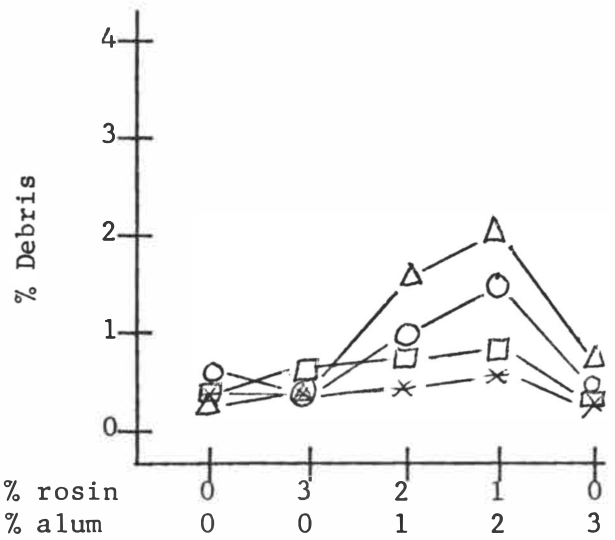


Figure 23: Coated paper containing 25% latex and 75% starch as binders. Repulping time=90 sec, pH=7, and temperature=50°C.

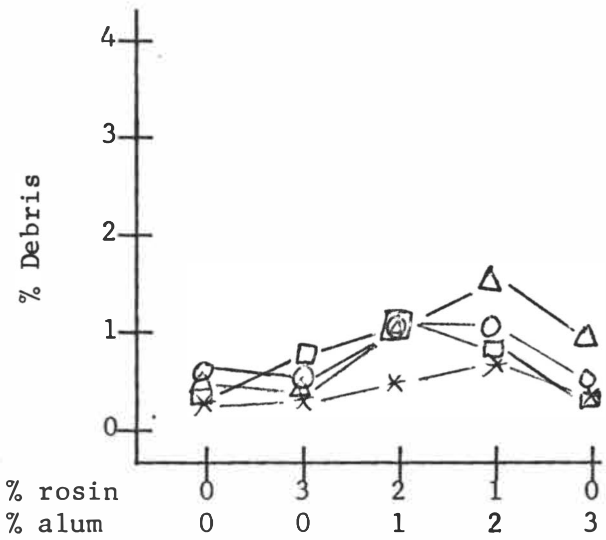


Figure 24: Coated paper containing 25% latex and 75% starch as binders. Repulping time=150 sec, pH=7, and temperature=50°C.

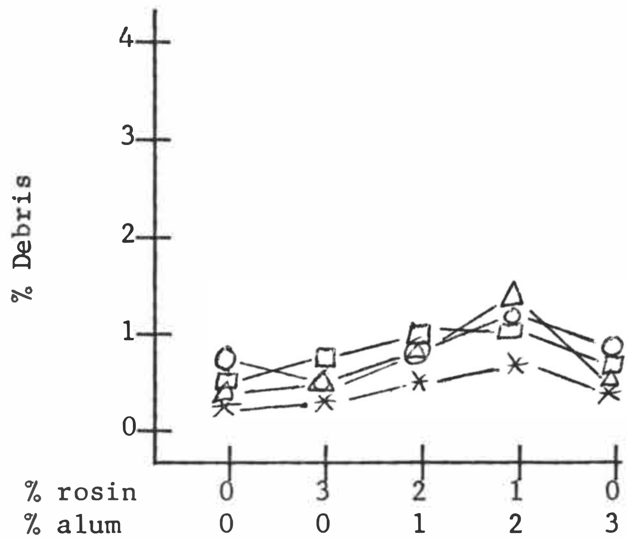


Figure 25: Coated paper containing 100% latex as binder. Repulping temperature= 20°C, pH=7, and time= 90 sec.

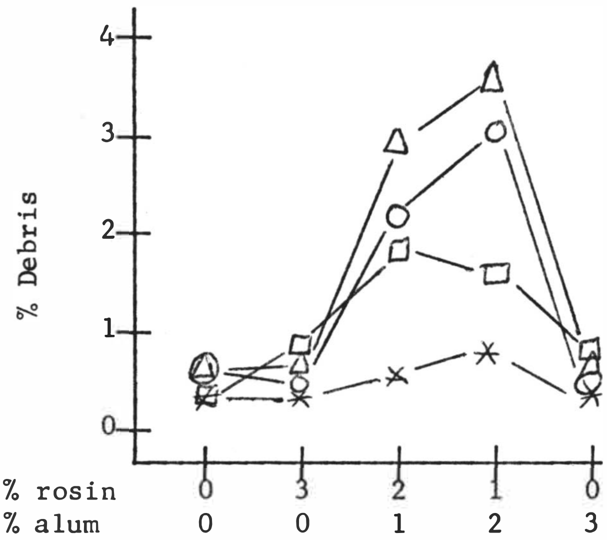


Figure 26: Coated paper containing 100% latex as binder. Repulping temperature= 50°C, pH=7, and time= 90 sec.

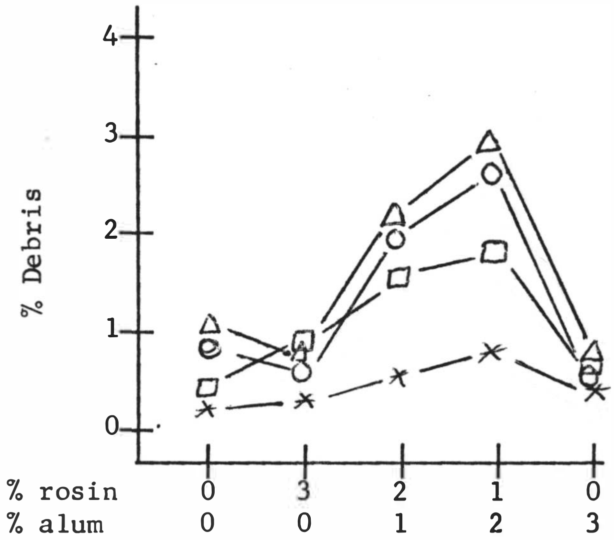


Figure 27: Coated paper containing 100% latex as binder. Repulping temperature=80°C, pH=7, and time=90 sec.

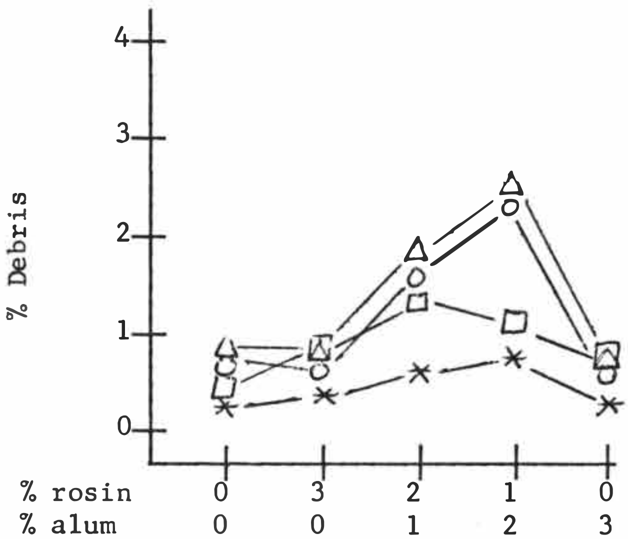


Figure 28: Coated paper containing 75% latex and 25% starch as binder. Repulping temperature=20^{o}C, pH=7, and time=90 sec.

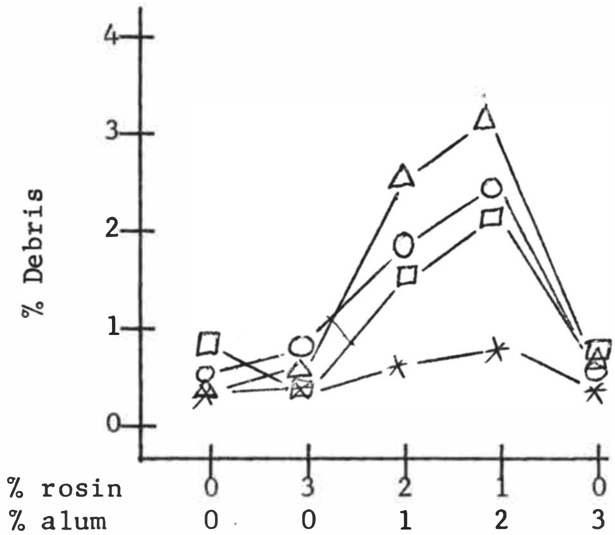


Figure 29: Coated paper containing 75% latex and 25% starch as binder. Repulping temperature=50^{o}C, pH=7, and time=90 sec.

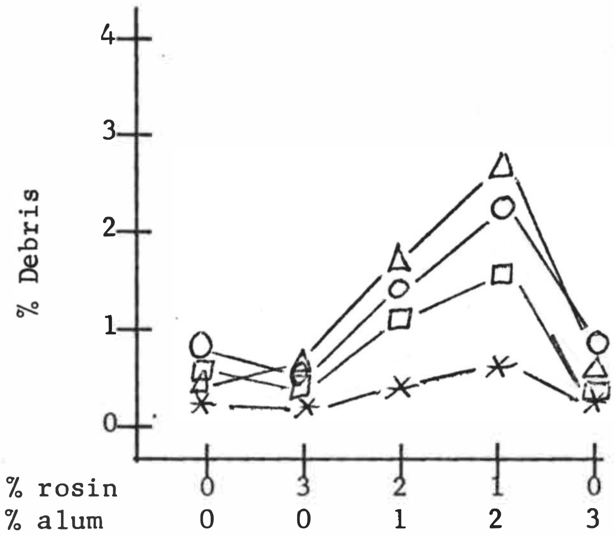


Figure 30: Coated paper containing 75% latex and 25% starch as binder. Repulping temperature=80^{o}C, pH=7, and time=90 sec.

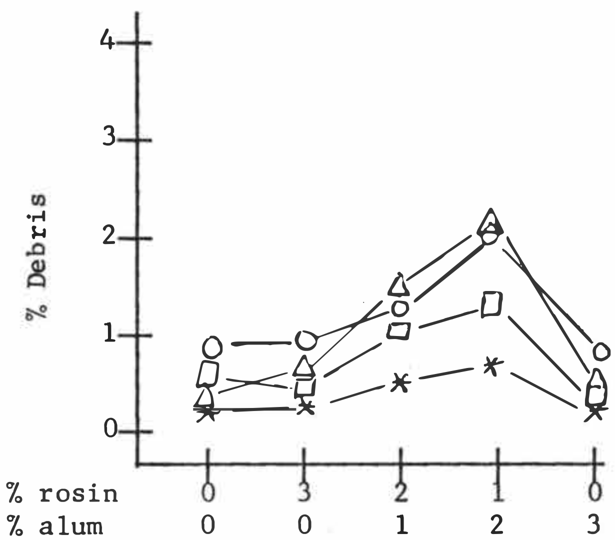


Figure 31: Coated paper containing 50% latex and 50% starch as binder. Repulping temperature=20°C, pH=7, and time=90 sec.

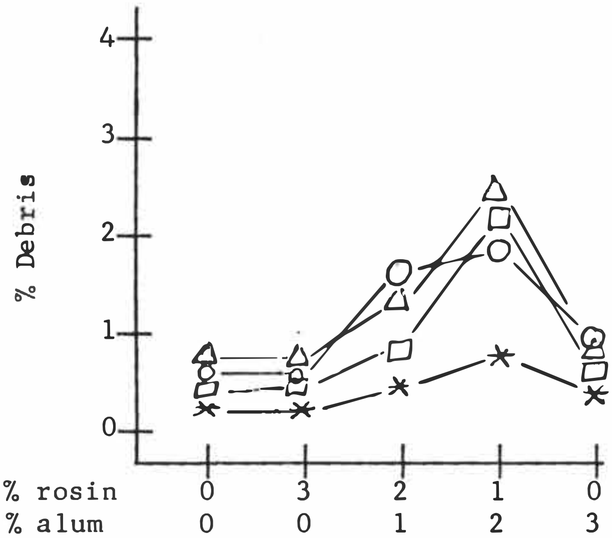


Figure 32: Coated paper containing 50% latex and 50% starch as binder. Repulping temperature=50°C, pH=7, and time=90 sec.

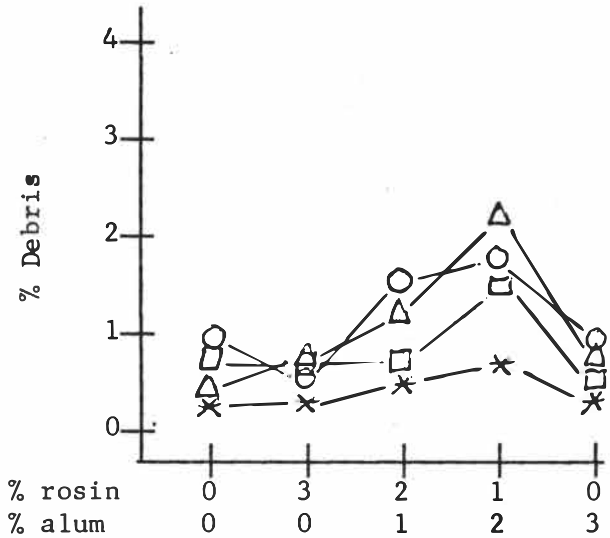


Figure 33: Coated paper containing 50% latex and 50% starch as binder. Repulping temperature=80°C, pH=7, and time=90 sec.

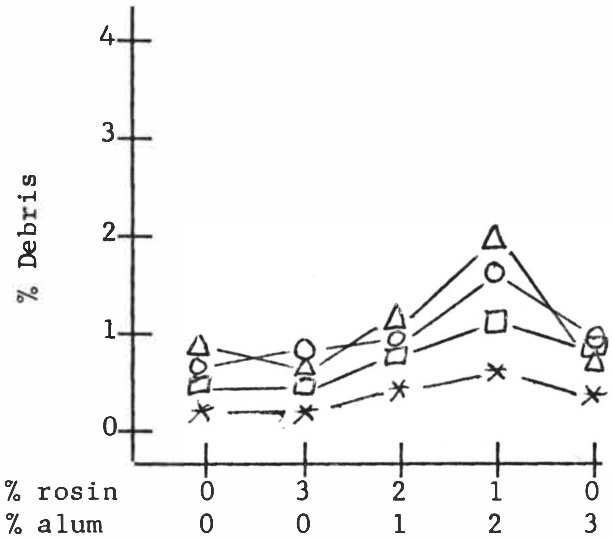


Figure 34: Coated paper containing 25% latex and 75% starch as binder. Repulping temperature=20°C, pH=7, and time=90 sec.

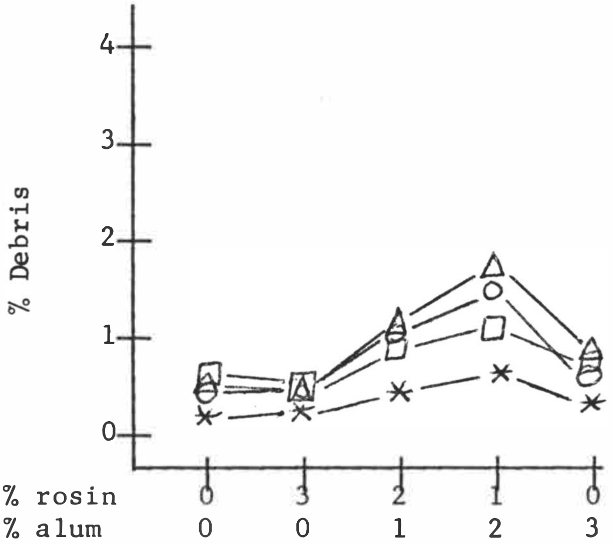


Figure 35: Coated paper containing 25% latex and 75% starch as binder. Repulping temperature=50°C, pH=7, and time=90 sec.

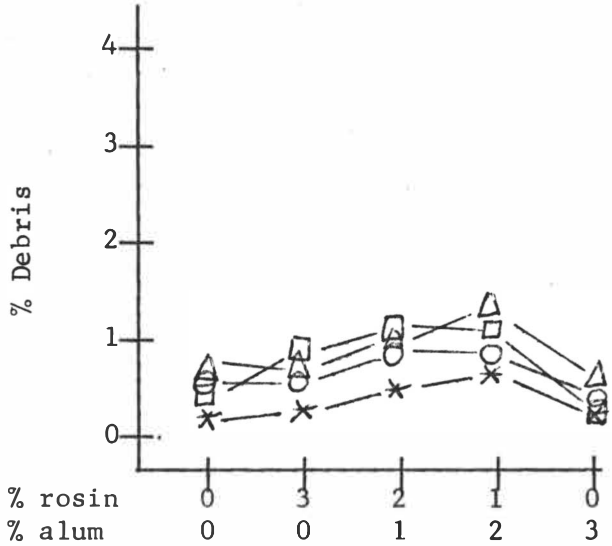


Figure 36: Coated paper containing 25% latex and 75% starch as binder. Repulping temperature=80°C, pH=7, and time=90 sec.

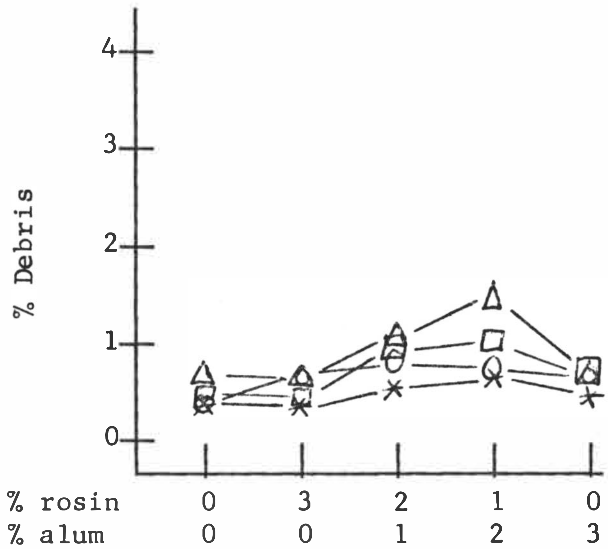


Figure 37: Coated paper containing 100% latex as binder. Repulping pH=5, temperature=50°C, and time=90 sec.

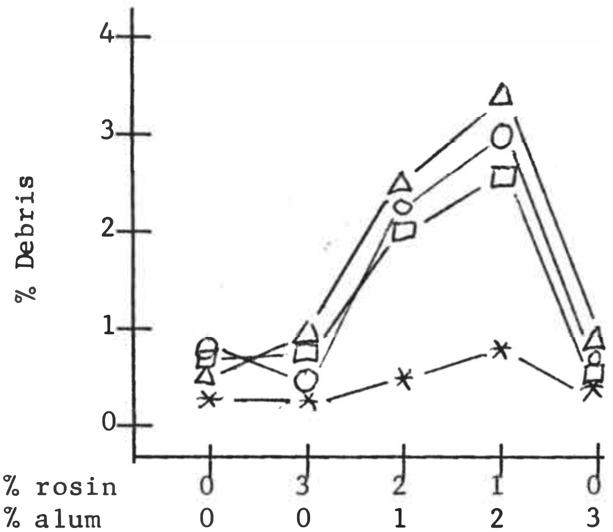


Figure 38: Coated paper containing 100% latex as binder. Repulping pH=7, temperature=50°C, and time=90 sec.

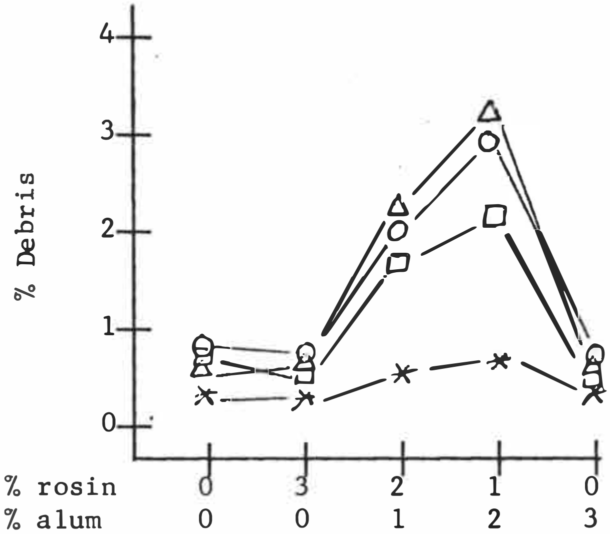


Figure 39: Coated paper containing 100% latex as binder. Repulping pH=9, temperature=50°C, and time=90 sec.

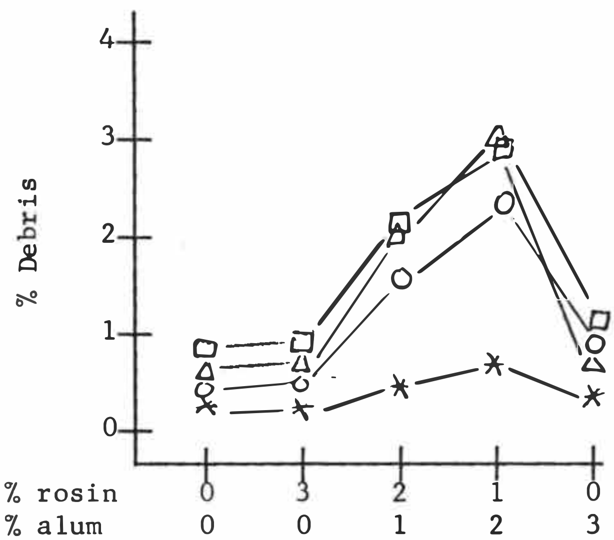


Figure 40: Coated paper containing 75% latex and 25% starch as binder. Repulping pH=5, temperature=50°C, and time=90 sec.

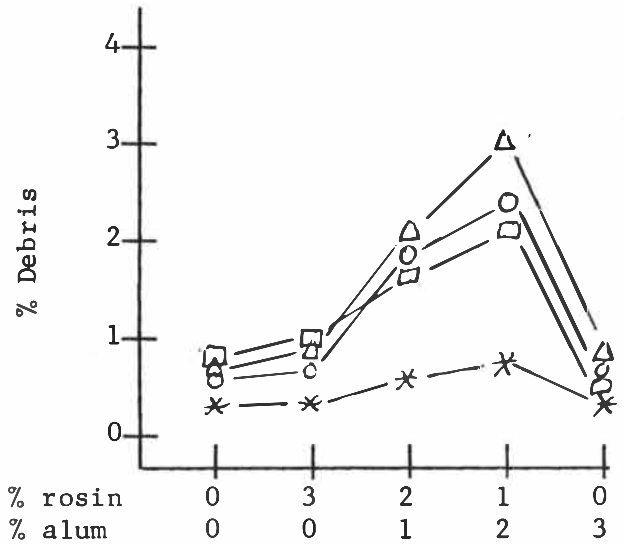


Figure 41: Coated paper containing 75% latex and 25% starch as binder. Repulping pH=7, temperature=50°C, and time=90 sec.

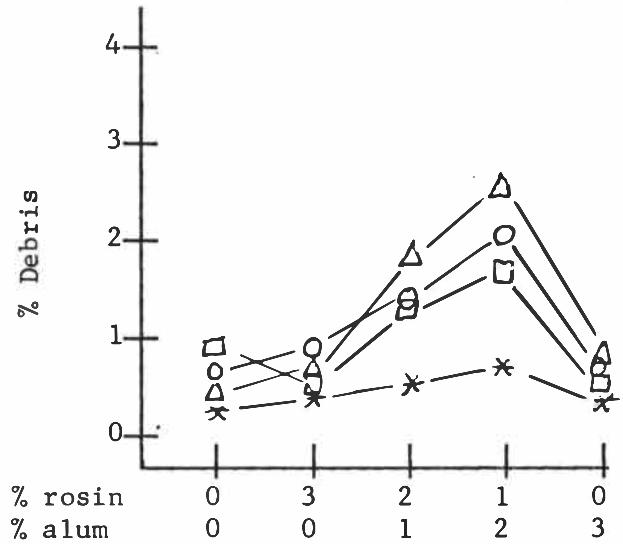


Figure 42: Coated paper containing 75% latex and 25% starch as binder. Repulping pH=9, temperature=50°C, and time=90 sec.

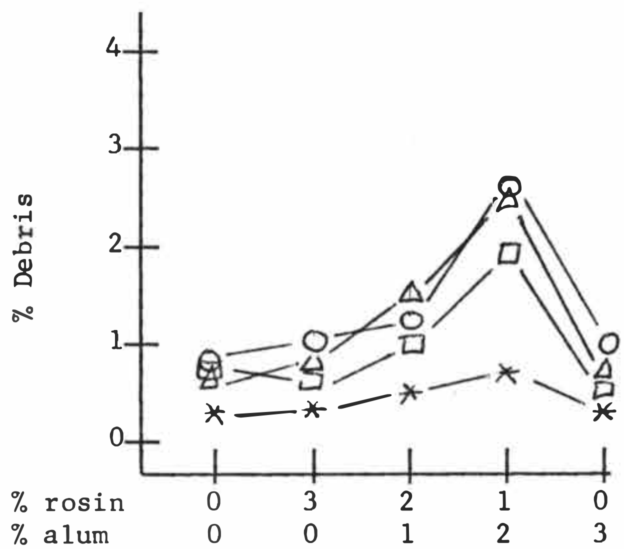


Figure 43: Coated paper containing 50% latex and 50% starch as binder. Repulping pH=5, temperature=50°C, and time=90 sec.

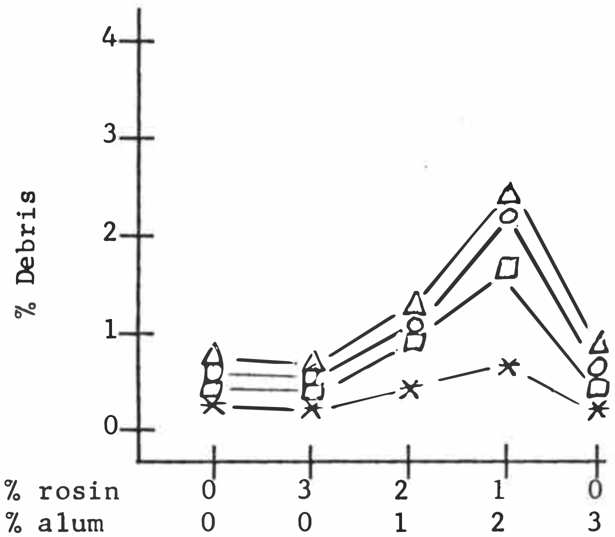


Figure 44: Coated paper containing 50% latex and 50% starch as binder. Repulping pH=7, temperature=50°C, and time=90 sec.

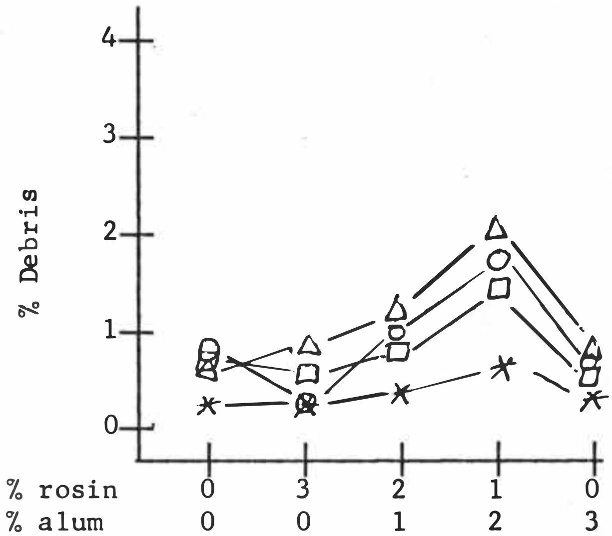


Figure 45: Coated paper containing 50% latex and 50% starch as binder. Repulping pH=9, temperature=50°C, and time=90 sec.

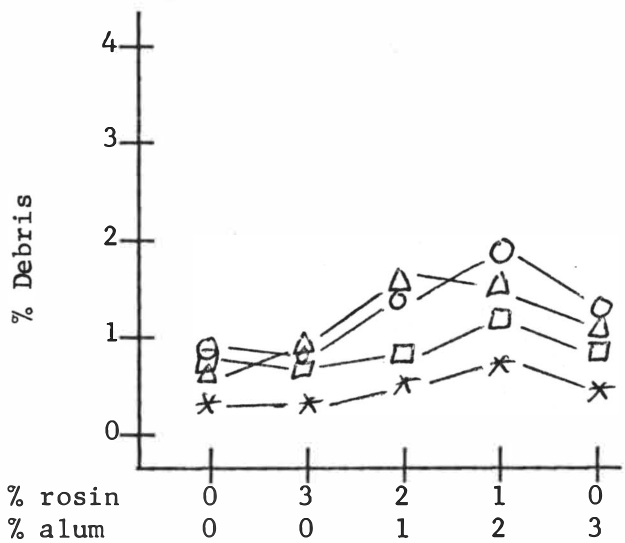


Figure 46: Coated paper containing 25% latex and 75% starch as binder. Repulping pH=5, temperature=50°C, and time=90 sec.

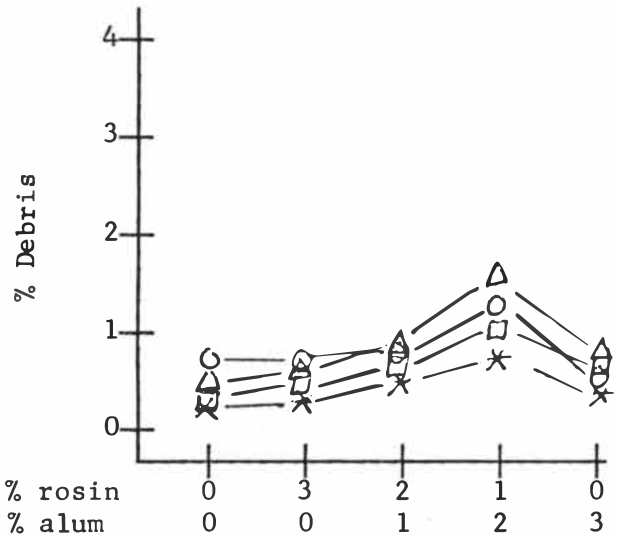


Figure 47: Coated paper containing 25% latex and 75% starch as binder. Repulping pH=7, temperature=50°C, and time=90 sec.

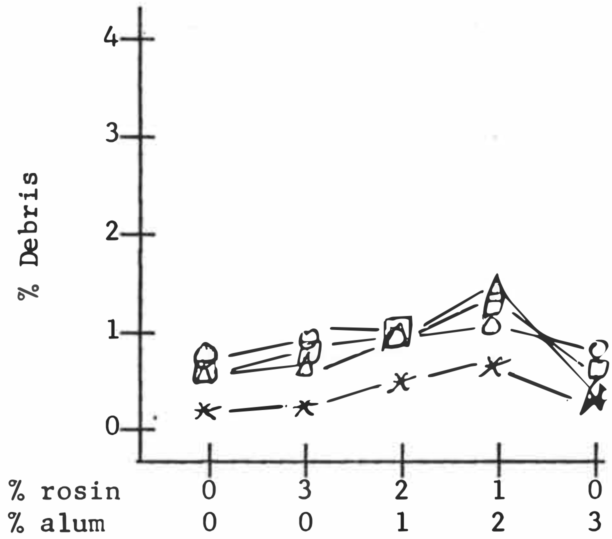
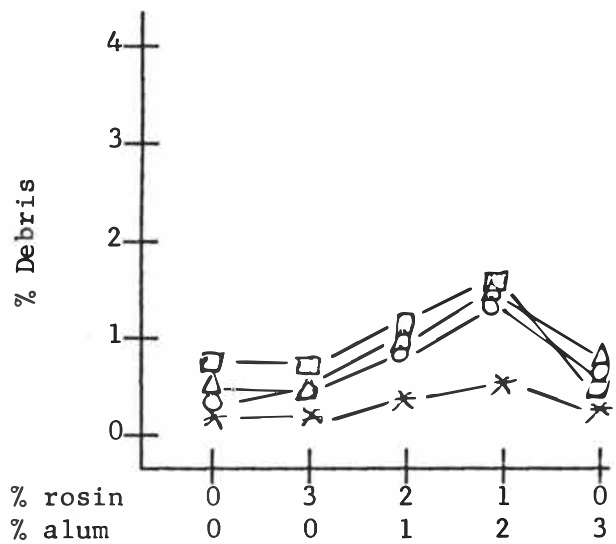


Figure 48: Coated paper containing 25% latex and 75% starch as binder. Repulping pH=9, temperature=50°C, and time=90 sec.



DISCUSSION OF RESULTS

From figures 1-12, which show the effects of time, temperature and pH on the repulpability of coated papers containing the three latexes studied, the following conclusions may be drawn.

The degree to which the stocks are repulped increases with time, temperature and pH. As each of these variables is increased, the amount of debris retained on the screen decreases, indicating the paper has been broken up more effectively. This dependency of repulpability on these variables is most pronounced at the higher percentages of latex addition, and decreases as the percentage of latex present decreases. This, along with the fact that the percent debris retained approaches 0% as the latex levels are decreased, proves that the repulpability of these stocks is directly proportional to the amount of latex present. The slopes of the lines all indicate that, when extrapolated to 0% retained, the variables of time, temperature, and pH could all be theoretically increased to give 0% debris retained on the screen; however, these conditions are limited by certain factors. At long times, power consumption is up and headboxes might run dry before the newly prepared stock reaches them. Temperatures must remain below the boiling point of water if open vessels are to be used. A pH too high, or too low, causes excessive chemical costs and degredation of the cellulose.

If the results in figures 1-4 are compared to those in 5-12, it is seen that repulping time is the most important factor in repulping these coated stocks. In the 100% addition levels of latex, for example, the difference in percent debris retained from thirty seconds to one hundred and

fifty seconds is 22% for SBR. For 100% PVAC, this difference is 13%. Compare these to 7% and 2%, respectively, for the same latexes with an addition level of only 25%. This again proves that the repulpability of these stocks is directly proportional to the amount of latex used as binder. In figures 5-8, the repulping temperature is varied. For 100% SBR and 100% PVAC, for examples, the percent debris retained for the former drops from 18% at temperature equal to 20°C to 9% at 80°C. For the latter, differences are 8% at 20°C and 3% at 80°C. Here again the effects are more pronounced at higher additions of latex than lower levels. This is significant when it is realized that the 100% starch sample left 0% retained. As the addition levels of latex approaches 0, there would have to be a smaller difference, because the percentages retained can go no lower than 0%. Since the starch blank yielded 0% retained in almost all cases, it is evident that the latex lines must be approaching the starch lines, again indicating the direct proportionality between amount of latex present and repulpability. The percentage differences for temperature are much less than those for time, but are greater than those for pH, therefore placing temperature as the second most important variable in repulping that was studied. In figures 9-12, repulping pH is varied. From these graphs the smallest differences in retained debris is present. In spite of these low differences, it still exhibits the same characteristics as the variables for time and temperature. Applying the same analysis for pH as for time and temperature, it is noted that pH is the least important variable of the three.

Since time is the most important variable, it appears that shear forces are important in disintegrating the paper. The longer it is left in the

repulping vessel, the more shear it is exposed to and more disintegration results.

Temperature effects the glass transition state of the polymer. At 20°C, which is below the glass transition temperature of the polymer, the polymer tends to be glasslike and brittle. As a result, the polymer is more likely to resist the shear applied by the impellor, since it cannot deform, thus making the impellor pulsate irregularly, and interfering with the full potential of the vector dependent shear forces. Until the polymer is broken up enough so the impellor can overcome this phenomena, the effect of these shear forces will be less than maximum. The temperature also helps wet the surface of the paper, increasing the diffusion of the water through the surface of the paper as the temperature increases. At this stage, agitation will not aid the diffusion. After the internal structure has been sufficiently wetted, agitation will aid in disintegration.

The pH of the system affects the tendencies of coagulation of the latexes. At the lower pH of five, the alkali sensitive latexes will coagulate, and will not repulp effectively. These larger particles get caught on the screen, increasing the percentage retained. The higher pH of nine keeps the broken up latex particles from agglomerating and interfering with the repulping system.

Upon examining these twelve figures, the SBR stands out as the most difficult latex to repulp under all of the conditions studied. The PVAC and acrylic are similar, with the acrylic being slightly easier to repulp. If the structures of these latexes are studied, it appears as though the carboxyl group present in the SBR increases its stability to chemical and

mechanical forces. The degree of carboxylation may be important; however, it was not the purpose of this paper to study this, as only one carboxylated latex was used. It is possible that the water insoluble nature of the latex makes it harder to disintegrate than the water soluble starch. This simple solubility difference may be important in determining repulpability. It is also possible as a theory, that the latex acts to fill in more voids in the coating because of its small particle size, than do clay or starch. As a result, the latex adds more binding power and breaks up harder. This would be so only if the latex did not interfere with the clay particles packing.

From figures 13-48, which show the effects of alum and rosin on the latex particles, the following conclusions may be drawn.

The amount of buildup on the rotating screen when the alum and rosin are added is a function of the particle size. This is shown by examining all of the figures. It is known from figures 1-12 that the SBR breaks up least, the PVAC, and then the acrylic latex. On nearly all of the figures, the SBR showed more buildup at the two levels at which both alum and rosin were present in the system. The PVAC showed the next highest buildup, and the acrylic showed the least buildup of all of the latexes. All of the conditions from figures 1-12 in which the latexes were broken up the least give the highest particle buildup and the conditions which repulp the best give the smallest debris buildup on the rotating screen.

Another significant fact was observed from examining the 100% starch sample. Even when this sample was introduced with the rosin-alum sizing system, a slight buildup did appear. If figures 1-12 are again examined, it is noticed

that the acrylic latex is almost repulped to the same degree as the starch blank. If the figures 13-48 are examined, especially figures 13-15, it is seen that the acrylic builds up to a much greater degree than the starch. This indicates a higher affinity of the rosin-alum to the latex over the fibers and the starch. The latex particle in water may have a larger negative charge than the fiber, so when the alumina reverses the charge on the rosin from minus to plus, the rosin would be attracted to the latex, and then the alumina anchors the rosin onto the particle. Another possibility is that the latex particles may have localized alkaline spots, which would force the rosin size precipitate to become isoelectric, which induces strong aggregation which could make larger particles that would get caught on the screen. The highest percentage of buildup occurred at 1% rosin and 2% alum. These conditions are close to operating conditions of an actual machine, where generally excess alum is used to insure that all of the rosin is converted from a minus charge to a plus charge and to make sure all of the rosin is anchored securely. At 2% rosin and 1% alum, less than 1% of the rosin is being changed from "minus" to "plus", compared to the full 1% in the first case, because of lost efficiency of alum due to excess rosin.

As is shown by the blank sample, and the samples where only rosin is present or only alum is present, there is a minimum buildup which will occur. Again this minimum buildup decreases as particle size does, again showing the dependency of this system on particle size.

In paper mills having a problem with buildup on dryers and wires due to latexes, it could be an intermediate size particle which is the problem. The very small particles would pass through the forming wire and into the

white water tray. The very large particles would get caught in the screens. A particle which is small enough to get through the screens but too large to pass through the wire would remain in or on the web. The latex particles, if on the bottom of the web, could either stick to or wedge into the wire, and build up there. If they are on top of the web and make it to the dryers, the sudden heat could melt them onto the dryers, where eventually a film could build up.

CONCLUSIONS

The repulpability of coated sheets is a function of the amount of latex in the sheet. The higher the latex content, the more difficult it is to repulp. Time is shown to be the most important variable in repulping. Repulping temperature is secondary to time, and pH is of least importance. The effects of latex containing coated papers is most evident at high levels of addition, but does exist at all levels. The SBR latex was most difficult to repulp, followed by PVAC, which is followed by the acrylic latex. The SBR was very difficult to repulp compared to PVAC and acrylic, which were very close.

The particle size of the partially dispersed coatings has a direct effect on the amount of debris caught on a rotating screen in the presence of alum and rosin as the sizing system. The larger the particle, the larger the amount of debris retained. The rosin-alum effect was most pronounced at 1% rosin and 2% alum addition levels. The rosin-alum effect was much greater on latex containing papers than it was on coated papers containing starch as the only adhesive.

It is possible that it is the intermediate size particles that cause build up problems on paper machines, not the very small or large particles. However, no specific data was obtained relative to this problem.

RECOMMENDATIONS

The study of the repulpability of coated papers containing latexes is important and deserves further study. As more and more synthetic binders come into use, inexpensive means of removing them or at least rendering them harmless to the rest of the papermaking process must be found.

A good place to begin further experimentation would be to study the effects of repulping on a specific group of latexes. For instance, take a group of SBRs with various degrees of carboxylation, and see what effects these have on their repulpability in coated papers. Next study a group in which all the latexes are derivatives of acrylic acid. Next study a group containing vinylic groups. I would recommend studying these groups because within each of them fall the most common types of latexes in use today. Another study for an advanced degree thesis would be to use an actual pilot machine, taking samples from key locations, and watching for any actual buildup. Then through use of chemical instrumentation, analyze the samples for latex content. This method would expose how much latex eventually ends up in the sheet. It would be a form of mass balance for the latex. Another study could include coating various grades of paper, from publishing down to newsprint, with only one type of latex in the coatings, and attempt to find out how base stock affects repulpability. Another study could introduce latex into a system of repulped paper, and using the Britt Jar, find out how these latexes affect drainage and retention aids. Also, study the effects of rosin-alum sizing on a single latex, using different types of fortified rosin, or unfortified rosin, sizes.

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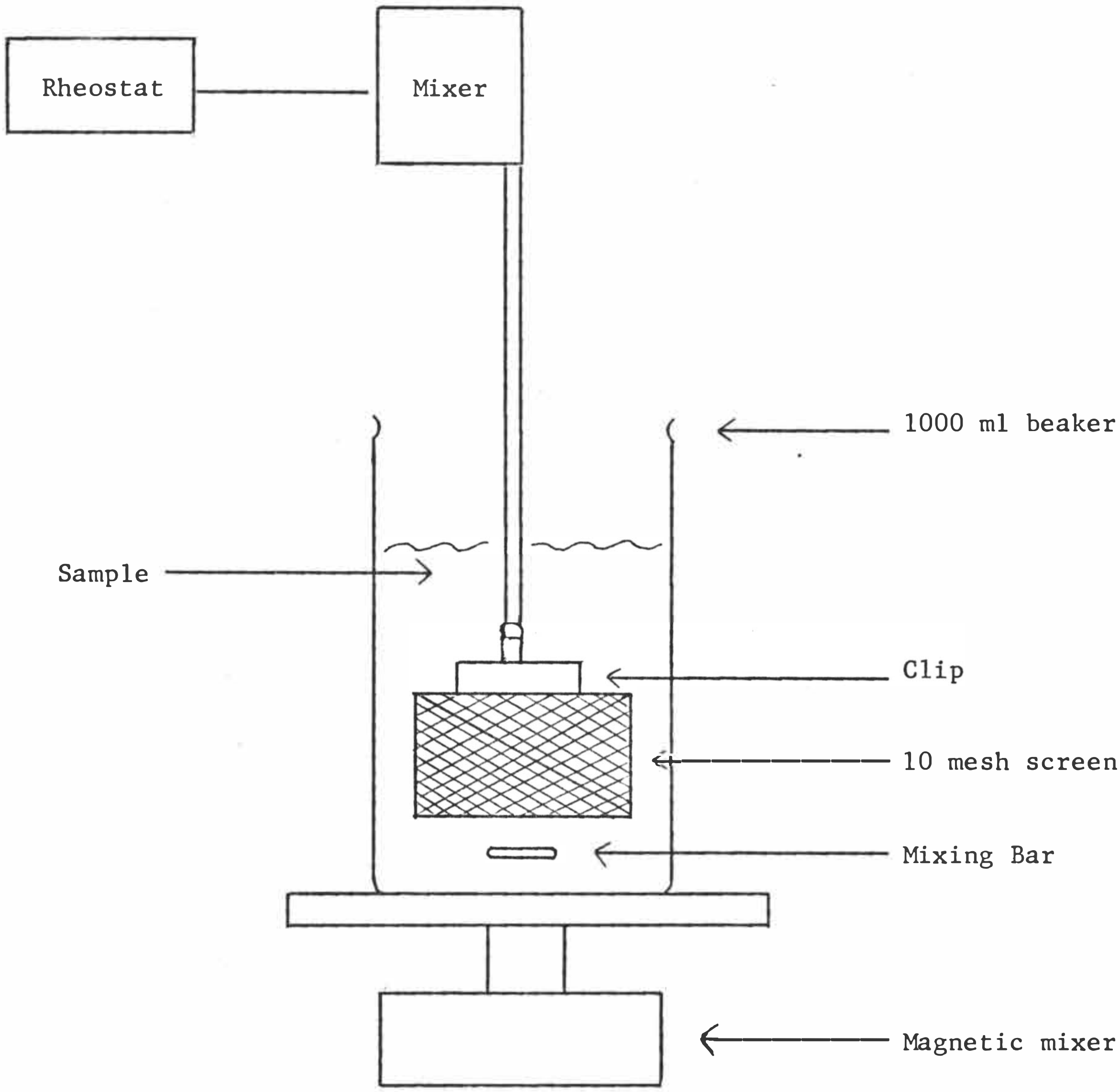
APPENDIX ONE

Apparatus for Dynamic Jar Evaluations of Repulped Stock



1) Screen and mixing bar rotate for 1 minute per sample

2) Sample size is 400 ml at .5% consistency

3) The screen is S-shaped to conform to walls of beaker

4) 2" x 4" rotating at 30 RPM, 10 mesh screen

5) Rotating same direction at 60 RPM, mixing bar

APPENDIX TWO

Actual Values of Percent Debris Retained on Screens

Stationary Method (Figures 1-12)

	Repulping Time (sec)			Repulping Temp (^{o}C)			Repulping pH		
	30	90	150	20	50	80	5	7	9
100% SBR	30.0%	13.3%	7.2%	18.0%	14.2%	10.0%	15.9%	14.9%	12.7%
75%	23.1%	11.6%	4.3%	15.5%	11.8%	7.7%	12.8%	11.5%	9.9%
50%	14.8%	8.1%	2.7%	9.0%	6.7%	4.1%	8.9%	7.3%	5.3%
25%	6.9%	2.5%	0.0%	4.7%	3.2%	0.9%	5.0%	2.8%	0.0%
100% PVAC	13.1%	7.3%	2.6%	8.1%	5.0%	2.7%	5.8%	4.9%	3.8%
75%	5.0%	2.6%	0.0%	5.7%	3.8%	3.0%	5.0%	4.5%	3.8%
50%	3.1%	1.6%	0.0%	4.1%	2.4%	0.9%	2.6%	2.1%	0.0%
25%	2.0%	1.0%	0.0%	2.0%	1.0%	0.0%	1.9%	0.6%	0.0%
100% Acrylic	5.0%	2.7%	0.0%	5.8%	3.9%	1.6%	3.5%	2.6%	2.3%
75%	2.6%	1.2%	0.0%	3.9%	2.0%	1.1%	2.5%	2.0%	1.8%
50%	2.5%	0.8%	0.0%	2.7%	1.0%	0.4%	1.3%	0.8%	0.0%
25%	1.6%	0.0%	0.0%	1.2%	0.0%	0.0%	0.0%	0.0%	0.0%
100% Starch	1.6%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%

APPENDIX TWO (CONTINUED)

Actual Values of Percent Debris Retained on Screens

Dynamic Method (Figures 13-48)

	Repulping Time (sec)			Repulping Temp (^{o}C)			Repulping pH		
100% SBR	30	80	150	20	50	80	5	7	9
0% rosin 0% alum	0.9%	0.7%	0.5%	0.7%	0.9%	0.9%	0.6%	0.7%	0.7%
3% rosin 0% alum	0.9%	0.6%	0.4%	0.8%	0.8%	0.9%	0.9%	0.6%	0.7%
2% rosin 1% alum	3.1%	2.2%	1.7%	2.9%	2.3%	1.9%	2.6%	2.4%	2.1%
1% rosin 2% alum	4.0%	3.3%	2.6%	3.3%	3.1%	2.6%	3.4%	3.2%	3.0%
0% rosin 3% alum	1.1%	0.9%	0.8%	0.8%	0.7%	0.9%	0.8%	0.6%	0.7%
75% SBR									
0% rosin 0% alum	0.8%	0.5%	0.5%	0.5%	0.6%	0.6%	0.8%	0.5%	0.6%
3% rosin 0% alum	0.7%	0.6%	0.7%	0.6%	0.7%	0.7%	0.9%	0.5%	0.7%
2% rosin 1% alum	2.7%	1.9%	1.4%	2.6%	1.9%	1.5%	2.2%	1.8%	1.6%
1% rosin 2% alum	3.6%	2.9%	2.1%	3.1%	2.8%	2.3%	3.0%	2.5%	2.2%
0% rosin 3% alum	0.7%	0.6%	0.6%	0.8%	0.7%	0.6%	0.8%	0.8%	0.9%
50% SBR									
0% rosin 0% alum	0.8%	0.7%	0.7%	0.8%	0.6%	0.9%	0.8%	0.6%	0.7%

Dynamic Method (Figures 13-48)

	Repulping Time (sec)			Repulping Temp (^{o}C)			Repulping pH		
50% SBR	30	80	150	20	50	80	5	7	9
3% rosin 0% alum	0.7%	0.6%	0.5%	0.9%	0.9%	0.6%	0.8%	0.8%	0.8%
2% rosin 1% alum	1.9%	1.4%	1.0%	1.5%	1.3%	1.1%	1.3%	1.2%	1.5%
1% rosin 2% alum	2.5%	2.1%	1.7%	2.4%	2.2%	1.9%	2.5%	2.2%	1.5%
0% rosin 3% alum	0.9%	0.7%	0.8%	0.9%	0.7%	0.8%	0.9%	0.9%	0.9%
25% SBR									
0% rosin 0% alum	0.4%	0.5%	0.6%	0.6%	0.8%	0.8%	0.3%	0.6%	0.5%
3% rosin 0% alum	0.5%	0.4%	0.5%	0.5%	0.8%	0.8%	0.4%	0.6%	0.5%
2% rosin 1% alum	1.6%	1.0%	0.9%	1.2%	1.1%	1.0%	0.9%	1.0%	0.9%
1% rosin 2% alum	2.1%	1.6%	1.2%	1.7%	1.4%	1.3%	1.8%	1.5%	1.4%
0% rosin 3% alum	0.9%	1.0%	0.6%	0.9%	0.6%	0.7%	0.9%	0.5%	0.9%
100% PVAC									
0% rosin 0% alum	0.6%	0.7%	0.7%	0.6%	0.8%	0.8%	0.9%	0.9%	0.6%
3% rosin 0% alum	0.5%	0.9%	0.6%	0.6%	0.7%	0.8%	0.4%	0.7%	0.6%
2% rosin 1% alum	1.5%	2.0%	1.1%	2.2%	2.0%	1.7%	2.4%	2.2%	1.7%
1% rosin 2% alum	2.6%	2.9%	2.1%	2.9%	2.7%	2.3%	2.9%	2.8%	2.4%

Dynamic Method (Figures 13-48)

	Repulping Time (sec)			Repulping Temp (^{o}C)			Repulping pH		
100% PVAC	30	80	150	20	50	80	5	7	9
0% rosin 3% alum	0.7%	0.8%	0.9%	0.7%	0.6%	0.9%	0.6%	0.8%	0.9%
75% PVAC									
0% rosin 0% alum	0.7%	0.9%	0.7%	0.6%	0.9%	0.9%	0.8%	0.7%	0.7%
3% rosin 0% alum	0.8%	0.9%	0.9%	0.8%	0.6%	0.7%	0.7%	0.8%	0.8%
2% rosin 1% alum	2.2%	1.7%	1.2%	1.9%	1.6%	1.2%	1.9%	1.5%	1.3%
1% rosin 2% alum	2.9%	2.2%	1.5%	2.4%	2.2%	2.1%	2.4%	2.0%	2.4%
0% rosin 3% alum	0.9%	0.8%	0.5%	0.6%	0.8%	0.8%	0.7%	0.7%	0.8%
50% PVAC									
0% rosin 0% alum	0.7%	0.8%	0.7%	0.9%	0.9%	0.8%	0.6%	0.7%	0.9%
3% rosin 0% alum	0.6%	0.9%	0.7%	0.6%	0.7%	0.8%	0.5%	0.2%	0.7%
2% rosin 1% alum	1.7%	1.2%	0.9%	1.7%	1.5%	0.9%	1.1%	1.0%	1.3%
1% rosin 2% alum	1.9%	1.2%	1.2%	2.0%	1.9%	1.6%	2.2%	1.9%	1.8%
0% rosin 3% alum	0.9%	0.6%	0.8%	0.8%	0.8%	0.8%	0.7%	0.9%	0.6%
25% PVAC									
0% rosin 0% alum	0.6%	0.6%	0.7%	0.8%	0.6%	0.5%	0.4%	0.7%	0.4%

Dynamic Method (Figures 13-48)

	Repulping Time (sec)			Repulping Temp (^{o}C)			Repulping pH		
25% PVAC	30	80	150	20	50	80	5	7	9
3% rosin 0% alum	0.5%	0.5%	0.5%	0.6%	0.6%	0.7%	0.4%	0.6%	0.5%
2% rosin 1% alum	1.2%	1.0%	0.8%	1.0%	0.9%	0.8%	0.8%	0.8%	0.8%
1% rosin 2% alum	1.5%	1.2%	1.1%	1.3%	1.0%	0.6%	1.4%	1.1%	1.1%
0% rosin 3% alum	0.6%	0.6%	0.9%	0.5%	0.4%	0.8%	0.5%	0.9%	0.9%
100% Acrylic									
0% rosin 0% alum	0.9%	0.7%	0.4%	0.4%	0.4%	0.6%	0.8%	0.7%	0.9%
3% rosin 0% alum	0.8%	0.7%	0.4%	0.8%	0.8%	0.9%	0.9%	0.7%	0.8%
2% rosin 1% alum	2.0%	1.3%	1.4%	1.8%	1.5%	1.6%	1.9%	1.6%	2.2%
1% rosin 2% alum	2.3%	2.2%	1.3%	1.6%	1.6%	1.4%	2.4%	2.2%	2.8%
0% rosin 3% alum	0.8%	0.8%	0.8%	0.7%	0.6%	0.8%	0.4%	0.6%	0.9%
75% Acrylic									
0% rosin 0% alum	0.7%	0.8%	0.9%	0.9%	0.6%	0.7%	0.8%	0.9%	0.7%
3% rosin 0% alum	0.8%	0.9%	1.0%	0.4%	0.3%	0.4%	0.9%	0.4%	0.5%
2% rosin 1% alum	2.0%	1.5%	1.0%	1.6%	1.2%	1.0%	1.6%	1.5%	1.1%
1% rosin 2% alum	2.1%	2.0%	1.4%	2.1%	1.5%	1.6%	2.0%	1.5%	1.8%
0% rosin 3% alum	0.6%	0.6%	0.5%	0.8%	0.5%	0.5%	0.4%	0.6%	0.5%

Dynamic Method (Figures 13-48)

	Repulping Time (sec)			Repulping Temp (^oC)			Repulping pH		
50% Acrylic	30	80	150	20	50	80	5	7	9
0% rosin 0% alum	0.4%	0.4%	0.6%	0.5%	0.9%	0.7%	0.5%	0.6%	0.7%
3% rosin 0% alum	0.5%	0.6%	0.4%	0.6%	0.7%	0.4%	0.5%	0.5%	0.6%
2% rosin 1% alum	1.4%	0.9%	0.2%	1.1%	0.9%	0.8%	0.8%	0.8%	0.6%
1% rosin 2% alum	1.4%	1.1%	0.8%	1.8%	1.6%	0.8%	1.9%	1.6%	1.2%
0% rosin 3% alum	0.5%	0.4%	0.5%	0.5%	0.6%	0.7%	0.5%	0.5%	0.4%
25% Acrylic									
0% rosin 0% alum	0.5%	0.4%	0.6%	0.6%	0.6%	0.4%	0.2%	0.6%	0.7%
3% rosin 0% alum	0.6%	0.7%	0.4%	0.5%	0.6%	0.7%	0.4%	0.6%	0.6%
2% rosin 1% alum	0.9%	1.1%	0.9%	1.0%	1.0%	1.0%	0.5%	0.8%	1.1%
1% rosin 2% alum	0.9%	1.1%	0.8%	1.1%	1.1%	0.6%	1.1%	1.5%	1.4%
0% rosin 3% alum	0.5%	0.4%	0.6%	0.7%	0.8%	0.4%	0.6%	0.6%	0.6%