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AN INVESTIGATION OF THE FEASIBILITY OF THE REPLACEMENT OF STARCH BY SYNTHETIC CATIONIC POLYMERS FOR THE EMULSIFICATION OF ALKENYL SUCCINIC ANHYDRIDE

by S
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A Thesis submitted in
Partial Fulfillment of the
Course Requirements for the
Bachelor of Science in Engineering Degree

Department of Paper Science and Engineering
Western Michigan University
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KEYWORDS

1) Alkaline Sizing
2) Alkenyl Succinic Anhydride
3) Emulsions
4) Hydrolysis
5) Hydrophobicity
6) Retention
7) Sizing

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number of keywords
used!

ABSTRACT

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The ofjective of this study was to determine the feasibility of replacing cationic starch with a synthetic cationic polymer in the emulsification of alkenyl succinic anhydride for use in alkaline sizing.

what hypothesis ?

Three methods of determining the validity of the hypothesis were investigated. The mechanisms encompassed with respect to polymer performance were emulsion stability, retention of ASA, and ASA hydrolysis.

Although a precise conclusion for the hypothesis was beyond reach during the course of study, important conclusions could be drawn upon completion of the experimental work about this relatively open area of study. Conclusions include: 1) Cationic starch which is presently used to emulsify ASA as a "protective colloid" appears to act as such only to mechanical shear and does not specifically provide chemical stability. 2) Shear applied in producing emulsions of ASA affects the ASA emulsion quality significantly. 3) Long chain polymers of high molecular weight are not a feasible alternative to starch using the specified emulsification procedure. 4) The procedure used to titrate for hydrolysis of ASA needs refining such that it could be reproduced in any laboratory before results are acceptable.

Not clear

It sound like the literature survey is incomplete.

The following literature review encompasses many areas which required further investigation in developing the objectives and experimental organization of this study. Areas investigated include sizing theory, chemistry of alkenyl succinic anhydride, and mechanisms involved in obtaining efficient sizing in paper and paperboard.

SIZING

references are in footnote order 1, 2, 3, 4

Sizing is generally defined as the addition of a chemical or chemical system to the wet end of the papermaking process which provides hydrophobicity or water repellancy to the final product. (8,12,16,42) Specifically, this defines internal sizing, as will be discussed here with no reference to surface sizing or massive barrier coatings.~~)~~ out * Sizing as supplied by the given definition provides only a temporary water repellancy to the paper, as the movement of liquid is only retarded and not completely stopped. (12,37) Wet strength test results are often falsely high due to the delayed wetting process inherent in a well sized sheet. Therefore, although it can appear as such, no wet strength is actually imp~~o~~arted to the sheet through sizing, only hydrophobicity. *

Unsized paper, being a porous structure of an extremely hydrophobic material (cellulose), is readily wetted by water and ~~other~~ aqueous fluids. Penetration of these liquids into the sheet can occur via two pathways. Penetration which occurs laterally between individual fibers and transversly through the pores in the web is termed interfiber penetration. That occurring within the fibers themselves is termed intrafiber penetration. Davison and Spurlin report general agreement with the theory that penetration initially occurs via pores and spacial openings between fibers, and is followed by intra-fiber penetration into the cellulose. (~~14~~ 6) However, certain size testing has indicated that the sequence is reversed. (~~22~~ 7) Gess offers that theoretically, it is possible for penetration to occur completely through the pores in the sheet and via no intrafiber penetration whatsoever. (~~19~~ 8)

?

"intra" or "inter"

Both modes of penetration are dependent on the rate of flow of a liquid through a capillary. This rate is then described by the Washburn equation^ which combines the Poiseuille equation * for laminar flow through a tube with the equation which represents natural fluid movement in a capillary tube. (~~14~~ 6) (See figure ~~one~~ 1)

The reference/introduction implies an equation which is not included in "Figure 1"

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etc.

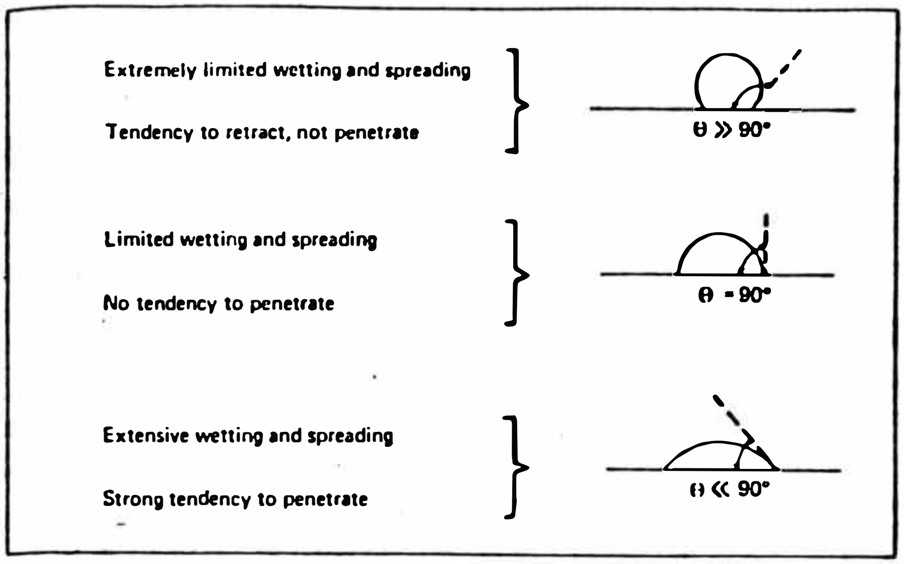


Figure 1*: Liquid flow through capillary (Washburn equation)
*taken from Davison (~~12~~ 2)

Four of the variables of the rate of flow are dependent specifically on the paper product and ~~it's~~ its final use. The dimensions of the pores are contingent upon basis weight, porosity, and bulk density of the product. (~~1~~2) Similarly, the surface tension and visc~~a~~osity of the penetrating fluid are controlled by the product's end use. Therefore, the last parameter is left to be controlled by the hydrophobicity provided by the sizing agent; that being contact angle. ✶

insert (?)

The sizing agent provides hydrophobicity by reducing the initially high surface energy of the cellulose which then causes high surface energy fluids to penetrate the paper at a reduced rate. (8) ? This is accomplished via an increased contact angle between the fluid and the paper's surface due to their respective energies. As the surface energy of the paper surface is reduced, high energy liquids form increasing contact angles. When contact angles greater than 90° form, the liquid tends to retract. At a 90° contact angle there is no tendency to penetrate and at angles less than 90° fluids have a strong tendency to penetrate the paper's surface. (4) ? (See figure ~~two~~ 2?)

To Figure 1

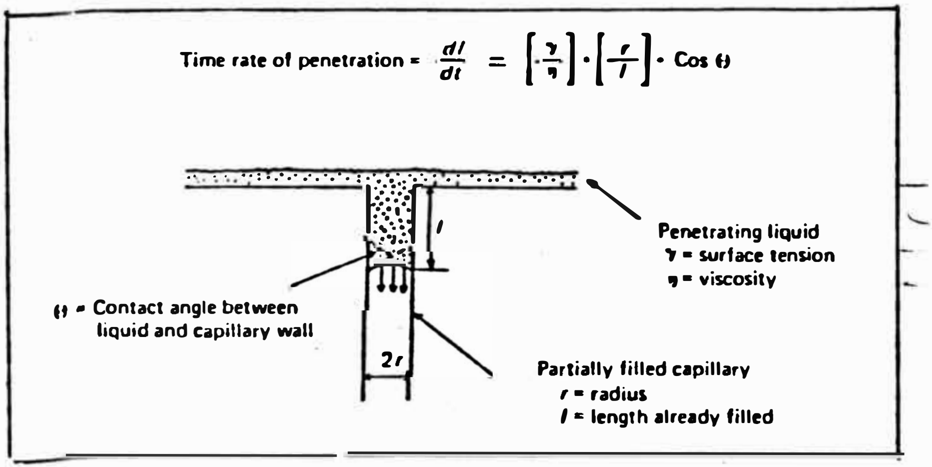


Figure 2*: Effect of contact angle on penetration of fluids through paper.

*taken from Davison (12) ?

Davison warns that all fluids, however, cannot be used to judge degree of sizing by contact angle. Although initially a fluid may form a high contact angle at the interface of the surfaces, some fluids and sizing agents react with one another to increase the paper's surface energy over time, reducing the contact angle. (12) ?

SIZING MEASUREMENT

The degree of sizing present in a given sheet of paper has been demonstrated to be highly dependent upon properties of the sheet itself and its end use. Measuring sizing in a sheet is also dependent on the test fluid and/or the specific test method.

50 50 (fifty not so)

Presently over so tests are available for the measurement of ☆

fifty (Spelled out)

sizing. "In general, the various tests are entirely contra-

~~(19)~~ ?

dictory in results."(10) Therefore, to get a true measurement of ☆ the efficiency of a sizing agent for application in different paper and paperboard grades, it would be most desirable to study the ability of sizing agent to perform the mechanisms necessary for good sizing rather than the sizing provided to one specific type of paper or paperboard.

Sentence Too long and Too Complex

The practical requirement for a successful sizing agent is to provide the sheet with hydrophobicity (via reduced surface energy of the fiber web ~~as discussed~~). In order to accomplish satisfactory sizing the sizing agent must also fulfill the following requirements:

1) It must have properties which allow it to be retained in the fiber system. (16) ?
2) It must be well distributed throughout the paper structure, covering fiber surfaces uniformly.
3) It must be permanently anchored to the fiber in some capacity.

4) The hydrophobic group of the size must be oriented properly, away from the fiber. (16) ?

5) Ideally, the sizing agent should have a high degree of chemical interness toward the penetrating fluid and have no negative affects on the papermaking process or the final product's physical properties. (12) ? SP ?

MECHANISMS OF SIZING

The requirements of a good sizing agent are performed differently depending on the sizing system. Conventional sizing in acid papermaking operations has been accomplished most commonly using rosin sizing for more than 170 years. (12) ? The effectiveness of rosin sizing is largely established at the wet end of the paper machine. Rosin and alum react in the wet end to form a precipitate. This process determines the cationic charge density and particle size which in turn controls the retention and distribution of size on the fiber. (16) ? The anchoring mechanism is provided by the electrostatic attraction between the hydroxyls of cellulose and the aluminum ion. (37) ? This mechanism is the "weakest link" in the rosin sizing process according to Dumas. (16) ?

In sizing with an alkenyl succinic anhydride emulsion, the anchoring process becomes the strongest mechanism with retention being the most difficult. Alkenyl succinic anhydride (ASA) is a cellulose reactive size introduced to the paper and paperboard industry in the 1970's.

incompatable ?

CHEMISTRY OF ALKENYL SUCCINIC ANHYDRIDE

To perform efficiently as a sizing agent ASA must obviously impart the physical property of water repellency to the final board or paper product. It is also desirable in many applications that some degree of sizing be obtained at or prior to the size press to allow smooth runnability through the surface sizing operation. Maher claims that due to the extremely high rate of reactivity with hydroxyls, sizing can be obtained at this point using ASA. (27)

However, the actual bonding of ASA to the cellulosic fines or fiber does not take place until the web travels into the dryer section of the machine. Electrostatic forces provide the mechanism by which size is retained in the wet end of the paper machine.

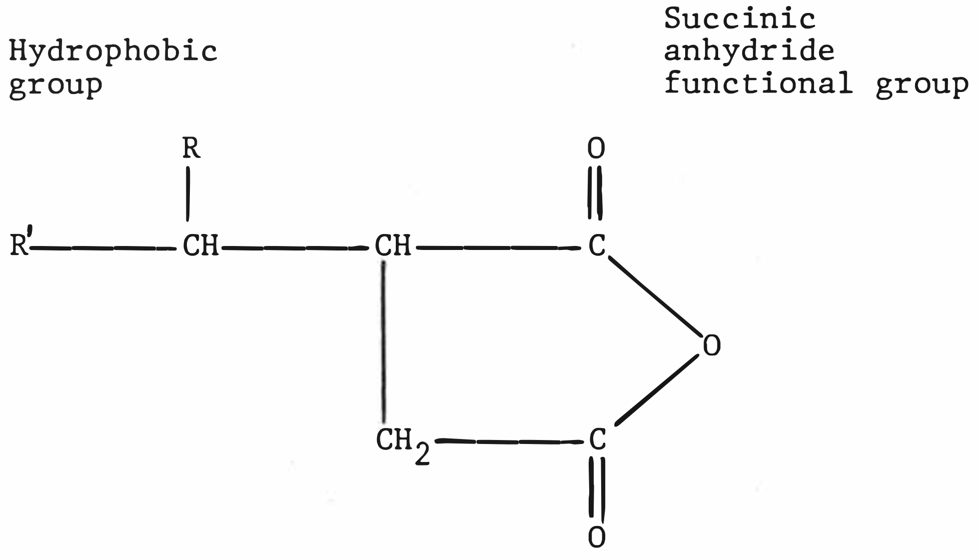
Retention of nonionic ASA (prior to the dryer section) in the anionic cellulose system is achieved by the addition of cations to the ASA prior to its addition to the stock. Conventional alkaline sizing systems commonly supply cationic charge by emulsification of the ASA with a cationic starch in a turbine pump at high shear rates (4,27) or by use of a chemical activator under low shear. (8,42) Starch used in this application acts as a protective colloid which allows the emulsion stability, reducing the rate of hydrolysis, a factor which will be discussed in considering sizing efficiency.

The cationic starch enters the fiber system with the ASA. This introduction of cations attatched to the essentially nonionic ASA into the anionic cellulose slurry initiates electrostatic bonding through depression of the electrical double layer surrounding the fibers and fines. (36) The ASA is thus retained covalent

prior to the dryer section where convalent bonding between the cellulose and ASA occurs exclusive of the cationic substance.

The source of cations is then, involved only in the retention of the ASA and not specifically in the bonding of the size to the fiber. In explanation of this bonding reaction it is necessary to review the basic structure of the ASA.

ASA, like nearly all sizing agents, is composed of a hydrophobic hydrocarbon group which attatches the size to the fiber. (14,16) This structure is clearly observed in Figure three, a diagram of the structure of alkenyl succinic anhydride.



*R and R' represent interchangeable hydrocarbon chains of at least five (5) carbons in length.

Fibure 3*: Structure fo an ASA size

*taken from Brink (8) and Wozniak (42).

out (mo n)

ASA is a "cellulose reactive size", forming a convalent bond between the fiber and the size molecule which is highly resistant to hydrolysis. (16,27) In the past sizing agents developed for use in the higher pH range had a tendency to interfer with fiber bonding, hence weakening the sheet. However, the convalent bonding which occurs as a result of the reaction between ASA and the cellulosic fiber actually produces a stronger fiber web. The reaction which occurs is expressed schematically as follows:

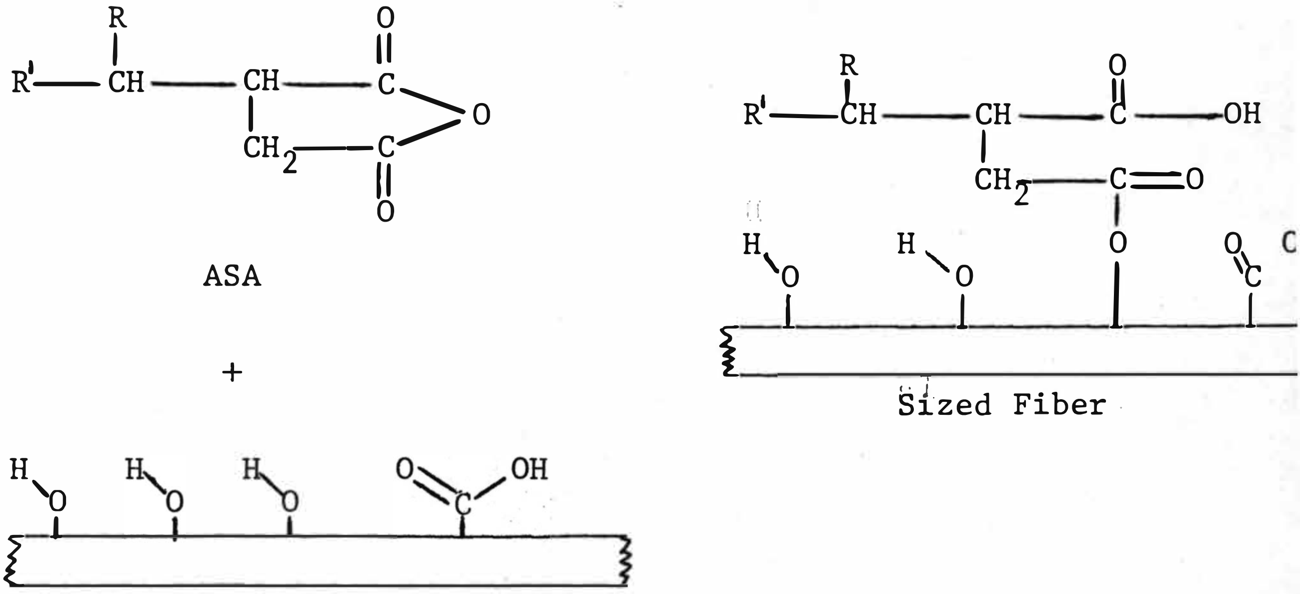


Figure 4*: Reaction of ASA with cellulose**

**taken from Brink (8) and ~~Kl~~Wozniak (42)

The size reacts with a hydroxyl group of cellulose, however it can also react with a hydroxyl of water. As mentioned previously, starch emulsified with the ASA acts as a protectant from this competing reaction known as hydrolysis.

The hydrolysis reaction produces hydrolazate, ~~an undesirable~~, an undesirable by product which is of little benefit in sizing. (42) When hydrolysis occurs, ASA molecules available for bonding to the cellulose are reduced and thus, the potential for sizing is also reduced. Proper emulsification of the

~~emulsification of the~~ emulsifier and ASA to produce a stable emulsion reduces the risk of sizing loss due to hydrolysis. (Emulsion pH should be approximately 3.5 to 4.0 to avoid hydrolysis prior to addition to the system. Hydrolysis of the emulsion is also promoted by increased temperatures, ~~the emulsion is also promoted by increased temperatures~~, the emulsion is most stable below 40°C and best at 25°C. (4))

Several techniques are employed in industry to insure proper emulsification of the size and cationic source including high shear applications using turbine emulsification pumps and low shear methods which use a chemical activator and an orifice or other static device. Often particle size and distribution are monitered during the trial stages of alkaline sizing systems to insure the emulsion has been manufactured properly. If the emulsion is produced correctly, the reaction between the ASA and cellulose should be optimized. However, initial retention of the ASA in the wet end of the paper machine must be high for the covalent bonds to occur in the dryers.

The point of addition and degree of mixing are pertinent to initial retention of ASA. Large degrees of shear tend to decrease ASA retention by knocking the ASA off the fiber, however, good mixing is essential to allow electrostatic bonds to form.

Retention of the ASA in the wet end occurs through a combination of coagulation and flocculation. The coagulation mechanism occurs during retention by electrostatic attraction between the ASA/cation emulsion and the cellulose fiber.

First pass retention of fiber and fines is also extremely important to the retention of ASA. Unhydrolyzed size which would be capable of bonding to the fiber in the dryer section can be lost on fiber and fines which are not retained.(27) Flocculation occuring within the system due to the bridging and patch mechanisms of polymeric retention aids fulfills retention requirements in this capacity.

The bridging model addresses the retention of fines and fiber via polymeric chains which attach themselves randomly to available adsoprtion sites on the surface of the suspended particles in the slurry. Portions of the polymer chain not attatched to adsorption sites on adjacent suspended particles, bridges are formed, and eventually a "three dimensional network" or floc.(24)

The patch model attributes particle aggregation to the electrostatic attraction occurring between negatively charged cellulose fiber and fines and cationic polymer "patches". Since the interaction force is highly dependent upon the localized patch charges, particles which have been partially neutralized by the cations need not be completely neutralized for aggregation to occur. (24) 23

EMULSION

The emulsion itself is very important to the nature of the sizing process and its effectiveness. The stability, particle size and particle distribution of ASA emulsions has been found to affect the ability of the size to provide hydrophobicity significantly. Thus, a basic understanding of the general properties of emulsions and factors pertaining to the stability of emulsions is necessary. The term emulsion is generally defined as a mixture of droplets or particles of two liquids which are immiscible. Commonly, one liquid is aqueous in nature and the other insoluble in water, giving rise to the terms by which emulsions are classified. Emulsions are referred to as oil in water, or water in oil depending on which liquid forms the continuous or outer phase and which liquid forms the non-continuous or inner phase. ASA emulsions are considered oil in water emulisons being that the continuous phase consists of the aqueous cationic starch solution.

Theoretically, emulison stability is increased greatly by reductions in the interfacial surface tension due to the large amount of surface area exposed in an emulsion. Real emulsions do not consist of perfect spheres as do the ideal emulsions to which the theory applies. Therefore, Adamson explains that real emulsions are governed by factors other than interfacial tension. The surface tension criteria for stable emulsions suggests stable emulsions should exist only when the inner phase volume fraction is less than or equal to 0.74 of the whole.(1)

ASA emulsions have been found to be stable and effective for alkaline sizing when the ratio of starch solution to ASA is 3:1.(~~2~~) (4) A surfactant property is necessary in making a stable ASA emulsion. ASA can be emulsified with surfactant immediately prior to its emulsification with starch on site, or it can be prurchased with the surfactant property previously manufactured into the product. *

Unpublished studies have shown that the particle size and distibution present in the emulsion is pertinent to the efficiency of the sizing process. It has been shown that emulsions perform most efficiently, are retained better, more well distributed, and hydrolyze at a reduced rate if the emulsion consists of uniformly distributed particles which are 85 to 90% less than 5 microns in size.

REVIEW OF PAST WORK

To the author's knowledge no previous work of the type proposed had been completed. The majority of the work done in attempt to study ASA and emulsions of ASA has been done by chemical suppliers of the size and is proprietary information. One study was done exploring the relationship of variable charge density starches and their effect on producing suitable emulsions, however, again the results were unpublished and proprietary.

In the past, the most common ASA emulsion has been, as previously mentioned, that produced using cationic starch as the continuous phase. There have been isolated cases in which water or cationic resins or promotors have been used to emulsify the ASA, incorporating cationic synthetic polymer retention aids to supply the necessary cationic charge to the system.(26) No specific claims to success accompanies these reports, and no cases of succesful use could be documented.

CONCLUSIONS

The preceeding literature review is a summary of factors affecting sizing using alkenyl succinic anhydride emulsions. ASA is used effectively as a sizing agent when emulsified in a turbine pump or homogenizer. Starch is often an undesirable however ~~in mill situatio~~

in mill situations due to reduced drainage rates and increased BOD leads often resulting from its use.

This study is intended to determine the feasibility of using synthetic cationic polymers to replace starch as the source of cations to the ASA molecules. Synthetic polymers have been found to be more efficient in providing drainage and limiting BOD loads than has starch. Such a system could allow the use of an efficient sizing system where it was previously impractical.

OBJECTIVE

Internal sizing is alkaline board and papermaking systems is presently being accomplished through the addition of a variety of different chemical additives. One of the most effective and popular methods employed achieves sizing via the addition of an alkenyl succinic anhydride (ASA) emulsion as idscussed. The most common ASA emulsion being used successfully at present is produced by the addition of ASA to a cationic starch solution under high shear (often a turbine pump), or in some instances, under low shear using a chemical activator. (Surfactant is emulsified with the ASA in a preliminary step if the ASA is not manufactured with surfactant properties inherent).

Many disadvantages occur as a result of employing starch as an emulsifier. In the past, little success has been experienced in using polymers as an emulsifying agent for ASA. However, some source of cationic charge must be introduced to the system to insure retention of the size.

Cationic polymers have been used to provide the necessary charge successfully although not as an emulsifier, but in a multistage application in which the ASA is emulsified with water and the polymer enters the system via an individual addition, separate from the emulsion addition point. (26) Such systems are complicated and not widely used as an alternative to starch emulsion systems.

Therefore, the~~s~~re exists a need ~~to~~ ~~for~~ to discover a cationic polymer which could effectively replace starch as an emulsifying agent which efficiently retains ASA on the fiber and fines without introducing the problems inherent with starch usage to the system. In an attempt to determine the characteristics of such a cationic polymer, it will be the objective of this thesis to determine the optimum combination of cationic charge density and molecular weight for retaining ASA size.

The objective stated has been drawn from a demonstrated need by industry for such a system. (4) Many paper and board mills have chosen to make the change to alkaline papermaking in the past decade, and among those, a surprising number have no facilities for the handling of starch in their mills. For these mills, there is not a large choice as to the sizing systems they are able to use, unless they are willing to install a starch system and employ the personnel to operate it. These mills must otherwise forfeit the choice of using an ASA sizing system, when in actuality, it may have been the optimum size for their operation.

Many mills ~~who~~ Which which presently operate without starch * have expressed ~~a~~ negative feelings toward the idea of the * installation and investment in the equipment and labor necessary to use starch in the mill. One major reason for these attitudes stems from the recolection that many papermakers have of the older, messier starch cooking systems which were once very common. Another reason takes root in that many papermakers believe that starch is a bad actor in efficient drainage (often with justification). Board mills are especially reluctant to add starch to their systems if it is not in use already due to the decreased drainage effect that it can cause. A third very solid reason for a mill to refuse starch usage is the environmental legislation to which they must adhere. Starch added to a system will increase the BOD load substantially, therefore making it absolutely impossible for the mill who operates very near their maximum BOD level to even consider its use.

It is obvious, then, that if an emulsion could be produced using an alternative synthetic emulsifying agent in place of starch an ASA system could be developed which could satisify a much larger realm of mills in the board and papermaking industry than is presently possible. Many mills who previously found the ASA sizing system highly effective, but unsatisfactory due to the role of starch, would have the choice of such a system without the complications of multistage additions.

EXPERIMENTAL

The design of an experiment to evaluate the polymers and their ability in effective sizing as the continuous phase of an ASA emulsion was complicated due to the large number of inconsistencies in testing for sizing. First, to date, no major chemical suppliers of ASA have claimed the ability to obtain consistent sizing in handsheets. One university study claimed a procedure to obtain such consistent sizing, but with no experimental data to back up such claims. Secondly, as presented in the literature review, sizing tests vary greatly depending on the paper product and test fluid and finally, contact angles studies depend on an extremely consistent and uniformly sized handsheet and possible chemical reactions which could occur between the sizing agent and test fluid. Therefore,

~~the i~~ [illegible]

the importance of testing the sizing agent's ability to provide the mechanisms previously presented as necessary for efficient sizing rather thab n sizing imparted to a handsheet.

The experimental evaluation of polymers began by first attempting to study the emulsions which could be produced using the emulsifiers. The ASA product chosen for use was one in which the surfactant emulsification step is unnecessary. The ASA is manufactured with surfactant properties such that the production be emulsified directly with the starch or other emulsifier. The brand name is Ac decosize 18. This product was chosen specifically for the property described to eliminate the surfactant or and its addition as a variable.

The polymers used were experimental products of another chemical company and specific data concerning these products is proprietary. The importance of selecting these specific polymers was were their interrelationship with one another rather than specifics. Six polymers were used; three being of the same mid-range molecular weight and increasing molecular weight. The significance in chosing this variety of polymers is to attempt to eliminate the possibility of obtaining incorrect results due to a narrow range of molecular weight or charge density polymers which could be accepted or eliminated as feasible starch substitutions.

Two starches were used as controls. Both are highly cationic starches used in the paper industry. The first, Accosize 72 is specifically for use in the emulsification of ASA, and the second Cargill "Charge Plus" is a cationic starch

starch used in industry as a wet end additive.

Water uas collected for use throughout the experimental procedure to insure constant PH, hardness and alkalinity, all of which have been known to affect sizing with ASA. (4)

The emulsification procedure used was obtained from a major supplier of ASA for alkaline sizing. The procedure is that which they use for laboratory work and have used for mill trials. This procedure was designed to simulate the shear received by the emulsion if it were to be emulsified by a single pass through a turbine pump. Slight modifications of the procedure to insure each emulsion was receiving precisely the same input energy in rpm's during emulsification. (For the specific emulsification procedure and illustration of the apparatus, please see Appendix, Figure A-1.)

Emulsions were each to be studied through microscopy to determine particle size and distribution and tendency for oiling and clustering of particles. The zeta meter was used to determine charge density and attrition over time. The emulsions were also to be titrated to determine the rate of hydrolysis over time. The hydrolysis titration procedure will be discussed in greater detail forthcoming.

Originally, microscopy alone was to be used to determine the state of the emulsion. Information concerning the state of the emulsion became available during the early stages of the experimental work.which made it necessary to make the addition of the charge analysis and rate of hydrolysis study. With the addition of these procedures, both of which are extremely time consuming, however time dependent also, the experiment would not be possible in the time alotted or without extra personnel.

Many starch emulsions were produced using the procedure and apparatus described. Microscopy studies were done on each emulsion under 470 X magnification to determine the particle size and distribution and charge analysis was run on several samples. Upon the realization of the time limitation of the amended experiment, another method of ~~e~~investigation was developed.

The second method of investigation was to attack the objective using a different mechanism of sizing as the prime variable of the study. Strazdins and Davison report independently that good retention of the size is one of the most important requirements of an efficient sizing system. (12,37) Retention of ASA in the system at the wet end is via electrostatic attractions between the cation attatched to the ASA molecule and the cellulose. The intent of studying the retention mechanism is to compare the ability of the polymers to retain ASA to the performance of the starch.

The Britt Dynamic Drainage/Retention Jar and Ultra violet spectroscopy were used to determine the fraction of ASA lost in the filtrate and by subtraction, that remaining in the jar. The Britt Jar has been used extensively to evaluate the performance of retention aids by simulating the turbulence occuring in the wet end of the paper machine. Filler, fiber, and fines retention are commonly determined using the Britt Jar. The procedure was modified slightly to determine the retention of the ASA.

The furnish used was 25% Canadian Hardwood and 75% Canadian Softwood, both bleached kraft. No filler loading was used. The fiber was refined to 403 points Canadian Standard Freeness in the laboratory Valley Beater. The screen used was the 125P, a 200mesh (75 micron) screen. A vaned chamber was used.and the voltage applied was kept low to provide only 300 rpm's such that excessive shear would not knock the ASA from the fiber completely.

A 500 ml sample of the diluted 0.5% stock was allowed to mix for 15 seconds. At this point the sizing emulsion (produced using the standard procedure) was added by syringe dropwise to provide the sample with 5.0 lb/T, as ASA to O.D. fiber. The sample was the allowed to mix for a period of 30 seconds, at which time a 50 ml sample was drawn and returned to the chamber to clear the area below the screen. The 100ml filtrate sample was then drawn for UV analysis. A trial of seven runs was made initially to determine whether a curve of the expected trend could be obtained using known amounts of ASA/starch emulsion and UV analysis.

The procedure for determining the ASA remaining in the filtrate incorporated the use of Ultraviolet spectrophotometry. No procedure could be obtained from any of the major suppliers to determine quantitatively such small amounts of ASA. The following method was developed in conjunction with the Chemistry department at Western Michigan University.

Anhydrides have an unusually high peak wavelength for UV spectrophotometry. (5) The sample collected from the Britt Jar was prepared specifically to attempt to remove all particles greater than 11 microns via filtration, leaving the ASA for analysis.

The 100 ml filtrate sample was first treated with surfactant. A 2.5 ml aloquot of 1% Tamol solution is added to the filtrate sample and mixed vigorously for 60 seconds. Upon completion of mixing the sample was filtered through paper allowing only particles less than 11 microns to pass through. From this treated sample three UV samples were taken and run in the UV spectrophotometer set at peak wavelength and absorption values were recorded. Curves of known quantities of ASA versus absorption were to be used to determine quantities present in the sample.

After obtaining no recognizable trend of the trials run in the plots of quantity of ASA versus absorption, the analysis method of the experiment was researched further.

It was then determined that the structure of ASA is such that analysis by spectrophotometry was not feasible. (4,5,42) Having such a structure, it was determined that the only feasible method to determine actual quantities of ASA after passage through the Britt Jar (in such minute quantity) was the use of radioactive tagging of molecules. This, the only method feasible , was not available in the laboratory in which the experimental work was done.

Another approach to fulfilling objectives was then necessary. The third investigation involved using the rate of hydrolysis titration procedure mentioned previously ot to study the ability of any of the polymers to provide protection against hydrolysis equal or better than that provided by the cationic starch.

The titration procedure is a proprietary procedure obtained for use(but not publication)from a major supplier of ASA. The procedure is time consuming and incorporates the addiiton of a chemical which is reactive with the unhydrolyzed ASA molecule. The quantity determined is express as percent of anhydride remaining. Many runs and variations of the starch emulsions wee done without ability to reproduce curves obtained from the same supplier of emulsion hydrolysis over time (for starch emulsions).(3) Altering pH and temperature, the two greatest factors affecting hydrolysis of ASA emulsions (3), did not alter the results of the results of the titration procedure. Starch concentration, emulsion ratio, and the blender container were among other changes made in attempts to reproduce the hydrolysis curves.

DISCUSSION AND RESULTS

The results obtained from the three methods of experimental investigation were not conclusive as to the feasibility of cationic starch replacemnet by synthetic polymers in the emulsification of alkenyl succinic anhydride for use in alkaline sizing. The area of study , however, being as open for research as it appears, was narrowed slightly by conclusions which were possible from the experimental work.

Through creating emulsions and studying their microscopy, the emulsification of ASA and any solution to act as the continuous phase can be refined. Although no specific trend with respect to the applied shear and the emulsion produced could be clearly defined. The results of the microscopy study showed that slight shear variations applied to ~~ot~~ the same components will produce very different emulsions.

Where some emulsions produced were of very uniform distribution and consisted of particles 90 to 95% less than 5 microns, other emulsions were grossly non-uniform and possessed particles ranging from approcimately 0.5 microns to 15 microns and even larger. Figure A-2 in the Appendix illustrates a "good" emulsion for sizing. The following Figure, A-3, is an illustration of an emulsion proven inefficient in sizing. (4)

It was also evident from observation during microscopy studies that the rate at which the ASA was added into the vortex and the uniformity of the addition also significantly affect final emulsion quality.

The charge analysis procedure appeared to be feasible method to monitor charge attrition, potential of the emulsion, and physical stability of the emulsion. The procedure, however, is time consuming and would require an entire study incorporating charge as the only variable.

During the initial stages of testing the emulsification procedure, it was determined that high molecular weight polymers would not emulsify. The polymers of this nature became a glue like substance in the emulsification chamber as shear was applied. It is possible that these polymers could react differently if emulsified through a static device rather than under high shear conditions such as those existing in a blender or turbine pump. It was evident that in using the described procedure for emulsification high molecular weight polymers are not an alternative.

The Britt Jar study suggests a feasible method of investigation of the ability of polymers to retain ASA in the wet end. However, the analysis method needs much investigation to determine a method to quantitatively measure small quantities of ASA in an aqueous liquid. The radioactive tagging of molecules is a possible method, but the procedure is complicated and inconvenient. If a better method of quantitative analysis could be developed and the previous one eliminated, the study could be much more extensive and reproducible.

In studying the abibility of polymers to provide a protective colloid, there was ~~limited~~ some evidence that the starch provides a protective colloid only to mechanical shear and not to the chemical stability of the ASA. During the experimentation, the pH and temperature, the two greatest factors found to affect the rate of hydrolysis (as previously mentioned) were altered extensively. After altering many other factors including starch concentration, the ratio of the inner phase to the continuous phase, and the emulsification chamber on the blender, the only factor which showed any alteration in rate of hydrolysis was the blender change. The change in blade and container dimensions dimensions would change the shear profile considerably. It appears that the mechanical change affected the hydrolysis rate whereas no chemical changes presented any change in hydrolysis.

The results of the titration procedure, however, regardless of the changes made, indicated that the titration procedure is not reproducible due to the inability to reproduce the starch curves of hydrolysis over time.

CONCLUSIONS

Conclusions drawn from experimental work include:

1) Shear rates applied in creating emulsions of ASA as the inner phase significantly affect emulsion quality.
2) Emulsion quality is also affected by rate and uniformity of the introduction of ASA into the continuous phase.
3) High molecular weight polymers are not a feasible alternative for starch in the emulsification of ASA.
4) The hydrolysis titration procedure incorporated needs to be refined such that reproduction in ~~in~~ any laboratory is possible.
5) It appears that the starch acts as a protective colloid only to mechanical shear and does not specifically provide chemical stability.

RECOMMENDATIONS FOR FURTHER RESEARCH

1) An investigation of the effects of shear on the emulsification process.
2) Study individually the ability of ASA/starch emulsions to provide the mechanisms necessary for efficient sizing agents as listed.
3) A refinement of the titration procedure for rate of hydrolysis or the development of a ne procedure.
4) The development of a procedure to measure minute quantities of ASA in aqueous solutions.

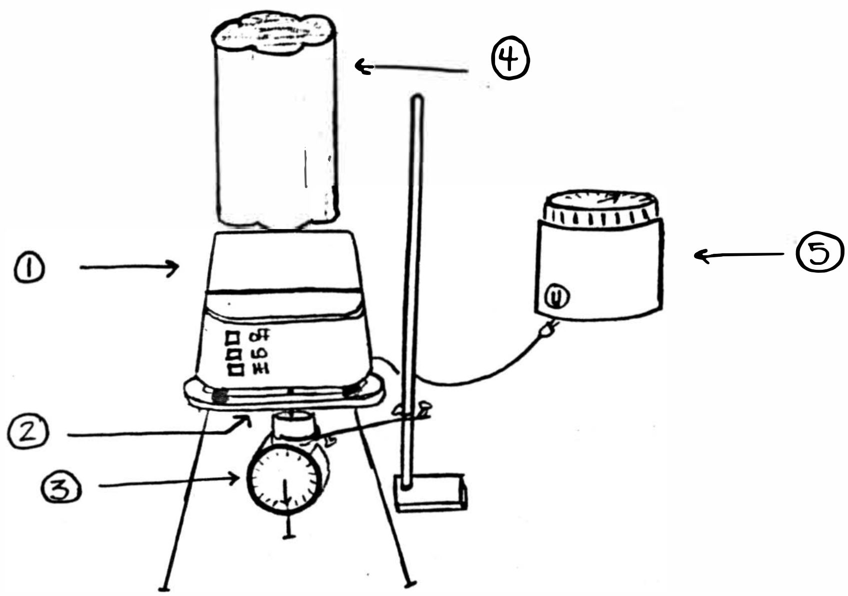
APPENDIX

EMULSIFICATION PROCEDURE

Although the specific times, voltages, and rpm's used in this procedure are proprietary, the procedure used follows. The emulsification was carried out using a Waring blender designed such that a tachometer could be mounted beneath it to measure rpm's delivered by the motor continuously. Also, the blender was connected to a "Variac" voltage supply controller.

The continuous phase of the teh emulsion (starch or polymer) was made up using the standard water at 3% and stirred in the blender at a specific rate for a specific time period. Over this time ASA was added drop-wise by syringe into the vortex such that the ratio of emulsifier to ASA was 3:1. Upon completion of ASA addition, the Variac was used to increase the voltage and thus rpm's to a constant level and run for a specified time period.(19)

FIGURE A-1
EMULSIFICATION EQUIPMENT SET-UP



1. Waring Blender
2. Rotating Tachometer Head
3. Tachometer Gauge
4. Emulsification Vessel
5. Variac Voltage Control

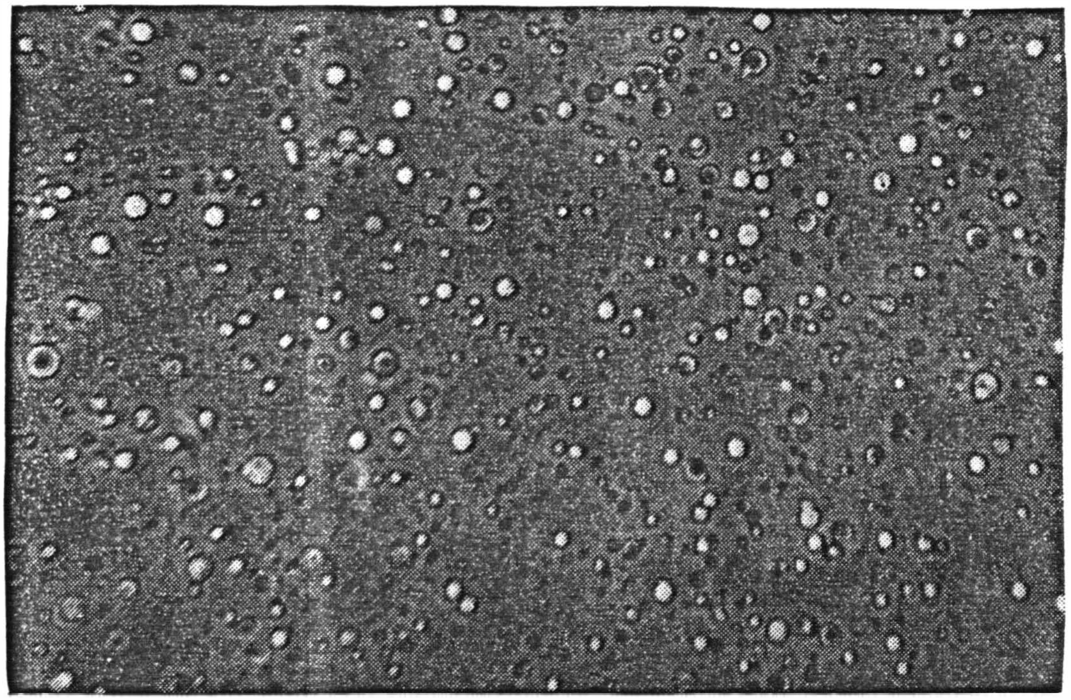


FIGURE A-2: "Good" Emulsion

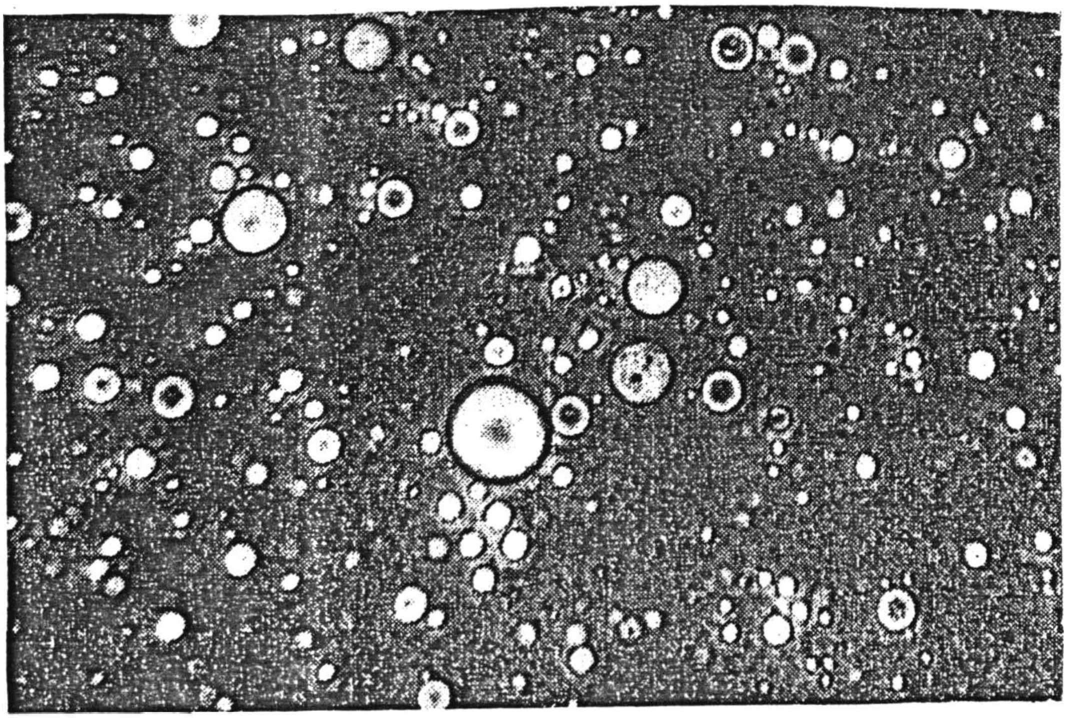


FIGURE A-3: "Poor" Emulsion

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