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Impact of Aluminum Chemistry and Order of Addition on Anionic Polyacrylamide Dry Strength Resins

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Impact of Aluminum Chemistry
and
Order of Addition on Anionic
Polyacrylamide Dry Strength Resins

by

Sally A. McKeel

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

Greater improvements in dry strength values can be obtained by maintaining the system's pH at the pH of precipitation formation, pHp. By using the pHp as the system's pH, more aluminum can be adsorbed onto the fibers. With more aluminum adsorbed onto the fibers, there are more possible interaction sites for the polyacrylamide to be fixed between the fibers; and thereby give a higher dry strength response.

An optimum level of polyacrylamide, .5% based on dry fiber, was used in achieving maximum dry strength effectiveness. When the order of addition of the rosin, aluminum species, and polyacrylamide system was varied, no significant differences in dry strength results were apparent.

KEYWORD INDEX

Polyacrylamide, aluminum, pH, bonding

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OBJECTIVE

This project will focus on the understanding of the aluminum chemistry and order of addition of polyacrylamides, rosin size, and aluminum cations as related to improvements in dry strength properties of the paper. Previous studies have varied the order of addition of these chemicals, but without a thorough understanding of the aluminum chemistry. This thesis will initially examine the understanding of the aluminum chemistry and then apply this knowledge while varying the order of addition of the rosin size, aluminum, and dry strength resin.

INTRODUCTION

Polyacrylamides were developed in the late 1950's as a pulp additive to improve the dry strength of paper and paperboard. Polyacrylamide added to pulp containing alum and rosin size has been found to increase the dry tensile, burst, and fold while also increasing the sizing response without changing the desirable sheet properties.

Alum or aluminum sulfate is the primary source of aluminum for most papermaking systems. Sodium aluminate and aluminum chloride are used in speciality grades. The aluminum cation is the key to obtaining good sizing and dry strength since the positively charged aluminum unites the cellulose fibers and rosin size which are both negatively charged.

Internal sizing of paper and paperboard is done to prevent penetration of aqueous liquids into the sheet. Rosin sizing is the typical internal sizing system. This thesis will investigate the interaction of aluminum cations, polyacrylamides, and rosin size to obtain excellent dry strength and sizing responses.

ALUMINUM CHEMISTRY

Before a review of the alum-rosin sizing complex and the role of polyacrylamide in the sheet, a basic knowledge of the aluminum chemistry must be completed. An understanding of the aluminum ion in aqueous solutions should aid in the understanding of the addition of polyacrylamide to the wet end of the paper machine.

Papermaker's alum, $Al_2(SO_4)_3$, is the primary source of aluminum for most papermaking systems. Sodium aluminate, $NaAlO_2$, and aluminum chloride, $AlCl_3$, are used in speciality grades. Until recently, fundamental knowledge of the role of alum and aluminum salts with other additives in the papermaking system has been inadequate. In studies of aluminum chemistry, the units used are moles per liter, M, whereas in the mill, the units are lb/ton of pulp on a dry basis.

pH is a critical variable in papermaking systems. Most mills operate in the range of pH 4.0 to 5.5 due to the benefits received from the aluminum in the system in this range (1). The effect of pH on adsorption of aluminum ions by cellulosic fibers can be seen from Figure 1 (2). Cations with the highest valence number adsorb onto the cellulosic fiber with a greater affinity for the carboxyl groups than divalent and monovalent

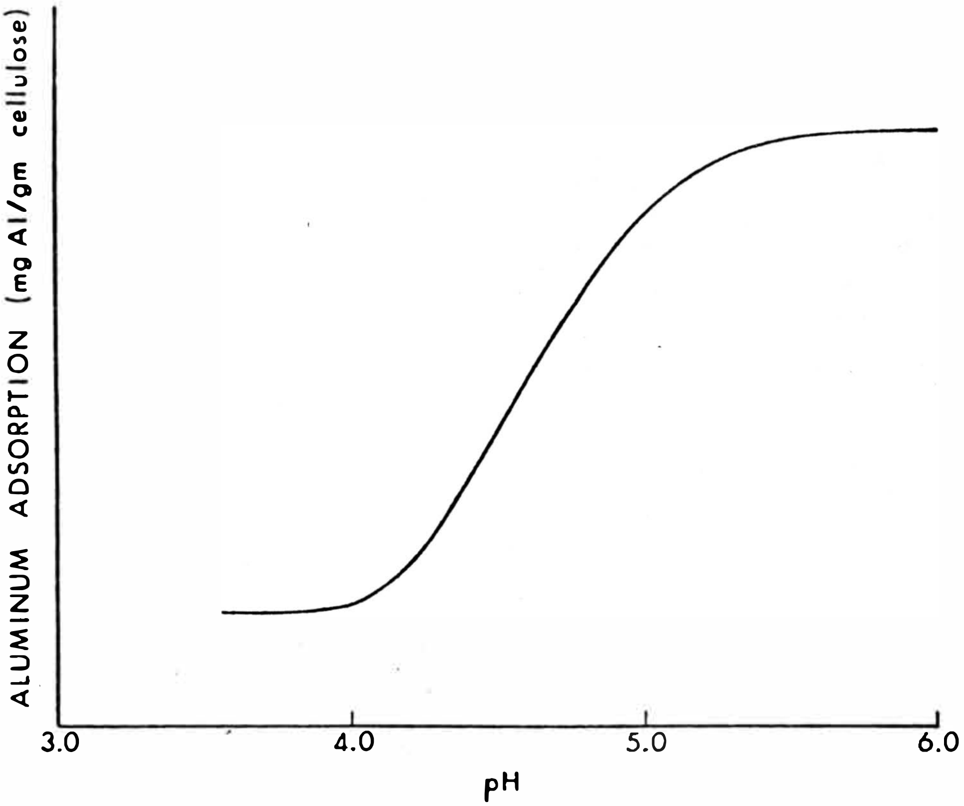


Figure 1. Effect of pH on Aluminum Adsorption

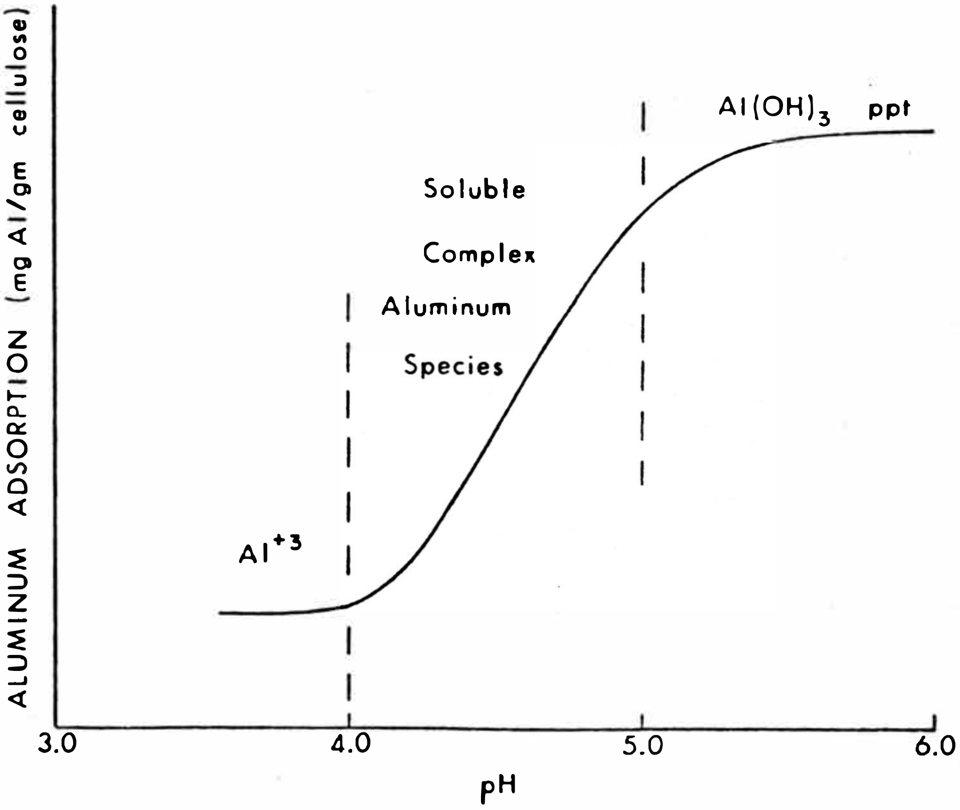


Figure 2. Effect of pH on Aluminum Adsorption and the Aqueous Chemistry of the Aluminum Ion

cations (Al^{3+}, Ca^{2+} Na^{+}).

From Fig. 1, the adsorption is constant below a pH 4.0, and reaches a plateau above pH 5.0. The increase in adsorption always occurs between pH 4.0 and 5.0. This adsorption is a function of pH and may be due to the carboxyl groups being ionizable, but it is also due to the aqueous chemistry of the aluminum ion (Figure 2) (2).

Figure 2 shows that below pH 4.0, the trivalent cation, Al^{3+}, is the predominant species. Above this pH, hydrolysis begins. When the hydroxide ion concentration increases, $AlOH^{2+}$ and other soluble hydroxo-aluminum complexes are formed. When the pH reaches above 5.0 and the concentration of hydroxide ions is high enough, $Al(OH_3)$- the insoluble aluminum hydroxide precipitate is formed.

Chemistry of Aluminum Solutions

Studies by investigators have been made on the hydrolytic reactions of aluminum. These studies on the aqueous chemistry of aluminum are complex and therefore have resulted in disagreements in certain areas, A major area of disagreement is whether or not the hydrolyzed aluminum species are monomeric or polynuclear. This disagreement can be attributed to the fact that aluminum solutions are very slow to approach a true equilibrium state so that meaningful data has been difficult to obtain.

The diversified chemical activity of the aluminum ion in aqueous solutions is a result of its high charge, 3+, and small ionic radius, 0.50 Å, which yields a high charge density (3,4,5). In order to reduce its high charge density, the aluminum ion acts as a Lewis acid electron pair acceptor and complexes with neutral or anion ligands. The aluminum cation complexes combines with six ligands to form the structure of Figure 3. The aluminum cation can form complexes with H_2O, OH^-, SO_4^{2-}, $H_2PO_3^-$, and $C_2O_4^-$, but not Cl^-, NO_3^-, and ClO_4^- (1). The H_2O and OH^- ligands can be discussed under the heading of aluminum hydrolysis.

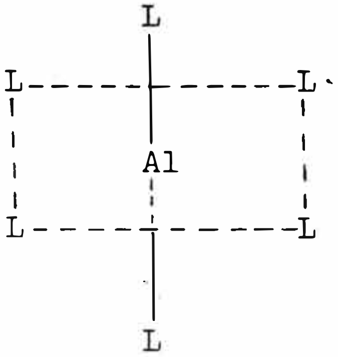


Fig. 3. Aluminum cation complexes with six ligands.

Aluminum Hydrolysis

Hydrolysis refers to the reaction of water with a cation to form soluble hydroxide or oxide complexes. At a pH below 3.0, when aluminum salts of a noncomplexing anion (Cl^-, NO_3^-, ClO_4^-) are dissolved in an aqueous solution, the trivalent hydrated cation, Al^{3+}, is formed. Above this pH, hydrolysis begins- the replacement of a water ligand with a hydroxide group. When the hydroxide ion concentration increases, $AlOH^{2+}$ and other hydroxo-aluminum complexes are formed.

$$\begin{array}{l} Al^{3+} + H_2O \rightleftharpoons AlOH^{2+} + H^+ \\ H^+ + OH^- \rightleftharpoons H_2O \\ \hline Al^{3+} + OH^- \rightleftharpoons AlOH^{2+} \end{array}$$

Fig. 4. Hydrolysis reactions.

Originally, Bronsted incorrectly proposed that the hydrolysis of aluminum occurred by a simple series of mononuclear complexes shown below in Figure 5.(6).

$$[Al(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Al(OH)(H_2O)_5]^{2+} + H^+$$
$$[Al(OH)(H_2O)_5]^{2+} + H_2O \rightleftharpoons [Al(OH)_2(H_2O)_4]^{1+} + H^+$$
$$[Al(OH)_2(H_2O)_4]^{1+} + H_2O \rightleftharpoons [Al(OH)_3(H_2O)_3]^{0} + H^+$$
$$[Al(OH)_3(H_2O)_3]^{0} + H_2O \rightleftharpoons [Al(OH)_4(H_2O)_2]^{1-} + H^+$$

Fig. 5. Simple series of mononuclear complexes.

Numerous workers have demonstrated that aluminum hydrolysis is not a simple mononuclear process. Instead, the hydrolysis complex, $AlOH^{2+}$, is in equilibrium with polynuclear complex species. Polynuclear species are formed when the mononuclear aluminum complex species are linked to each other by the hydroxyl bridging process called olation (2).

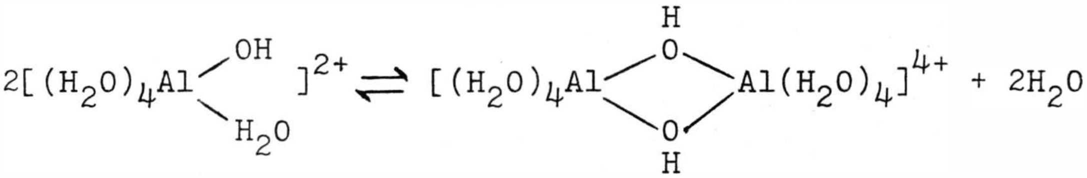


Fig. 6. Polynuclear species formation.

The size of the polynuclear complex species depends on how many times this olation process occurs. Various forms of the polynuclear species have been proposed by many workers in an attempt to understand how the aluminum ion behaves during hydrolysis. Hayden and Rubin have done the most complete analysis to date on aluminum hydrolysis and precipitation.

Hayden and Rubin's Work

Work by Hayden and Rubin (7) using aluminum nitrate concluded that only five aluminum species are present: Al^{3+}, $AlOH^{2+}$, $Al(OH)_3$, $Al(OH)_4^-$, and $Al_8(OH)_{20}^{4+}$. Their work suggests only one polynuclear species, $Al_8(OH)_{20}^{4+}$.

The distribution of the aluminum species as a function of pH is shown in Figure 7 (7). Notice that a small amount, less than 10% of the total aluminum fraction, exists as the mononuclear species, $AlOH^{2+}$. Also $AlOH_4^-$ occurs only in pH ranges above 8.0. A large amount of aluminum is used in forming the polynuclear species over a very limited pH range. The polynuclear species is in equilibrium with the precipitate so that the maximum concentration of $Al_8(OH)_{20}^{4+}$ occurs at the pH of precipitation formation or pHp.

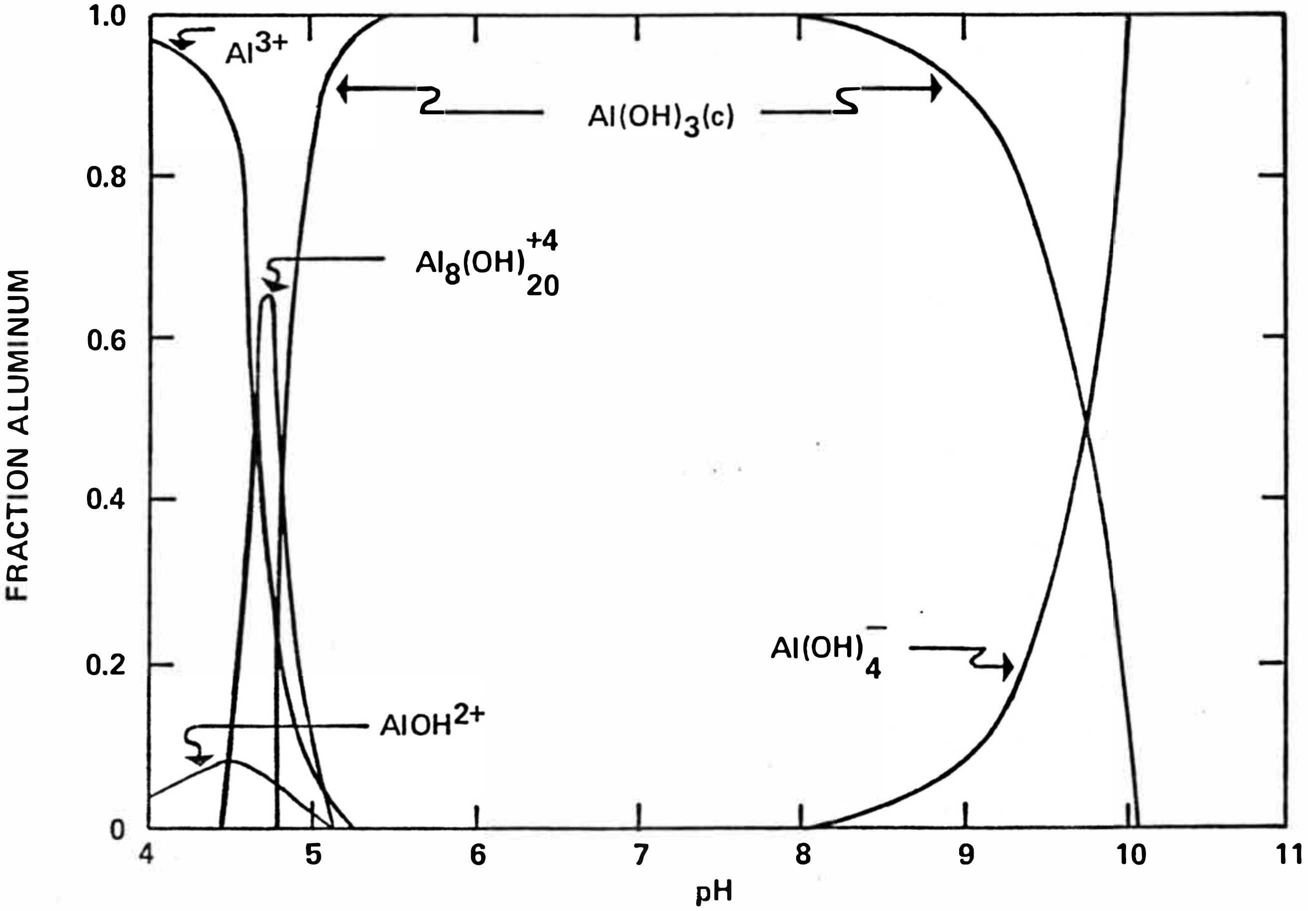


Figure 7. Distribution of Aluminum Species as a Function of pH

The distribution of the four aluminum species within the pH range of 4.0 to 5.5 can be seen in Figure 8 (7). From Fig. 8, three distinct regions of pH range can be observed. The first region is at the lower values of pH where only Al^{3+} and $AlOH^{2+}$ exist. In the middle region, the polynuclear species is formed, but this region is still below the pHp. In this region, Al^{3+}, $AlOH^{2+}$, and $Al_8(OH)_{20}^{4+}$ are present with the majority existing as Al^{3+} and the polynuclear species. The third region occurs above the pHp and concerns the aluminum hydroxide precipitate, $Al(OH)_3$.

The distribution of the complex aluminum species is a function of the aluminum concentration as seen in Figure 9 (7). The three regions stated above still exist, but have shifted. As the aluminum concentration is increased, the polynuclear species forms in greater amounts and at a lower pH. The pHp moves to a lower pH with an increased aluminum concentration causing all the distribution curves to shift to the left. Hayden and Rubin's work made an important point- that when studying the adsorption properties of aluminum slats, the pH and aluminum concentration of the system are interrelated, dependent variables.

Aluminum Complexes with Other Anions

The aqueous equilibria of aluminum from aluminum sulfate is considerably more complicated than aluminum nitrate due to the complexing effect from the sulfate ion. The sulfate ion is of interest since alum, the primary source of aluminum in the paper industry contains the sulfate ion. A complete

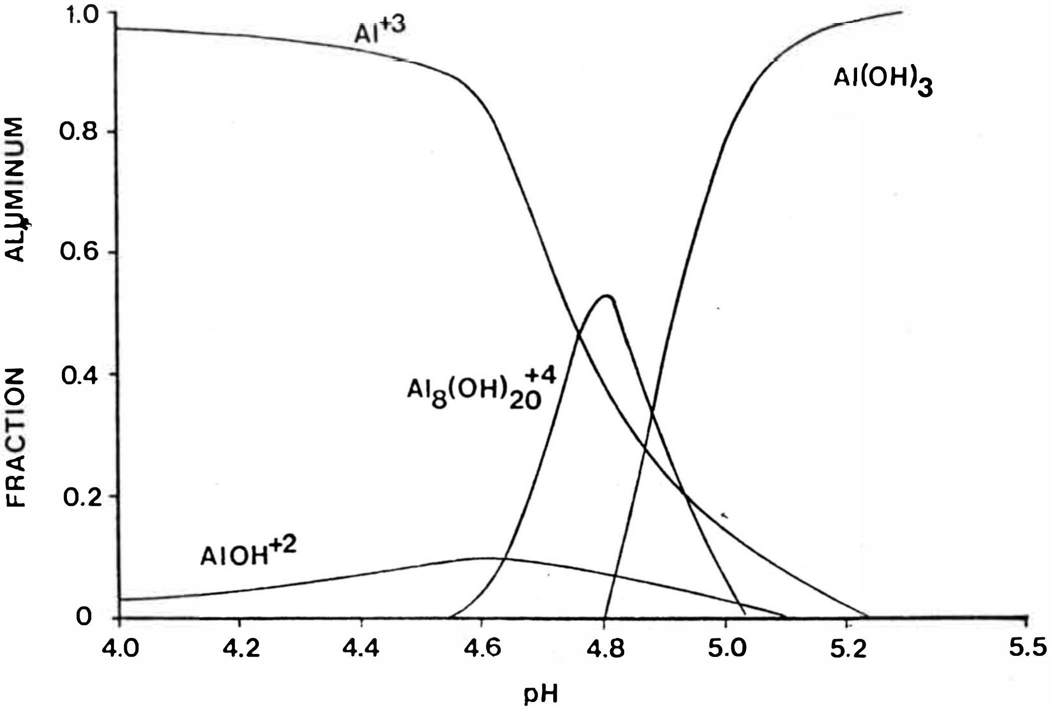


Figure 8. Distribution of Aluminum Species as a Function of pH at pH 4.0-5.5 (2.5 x 10^{-4} M)

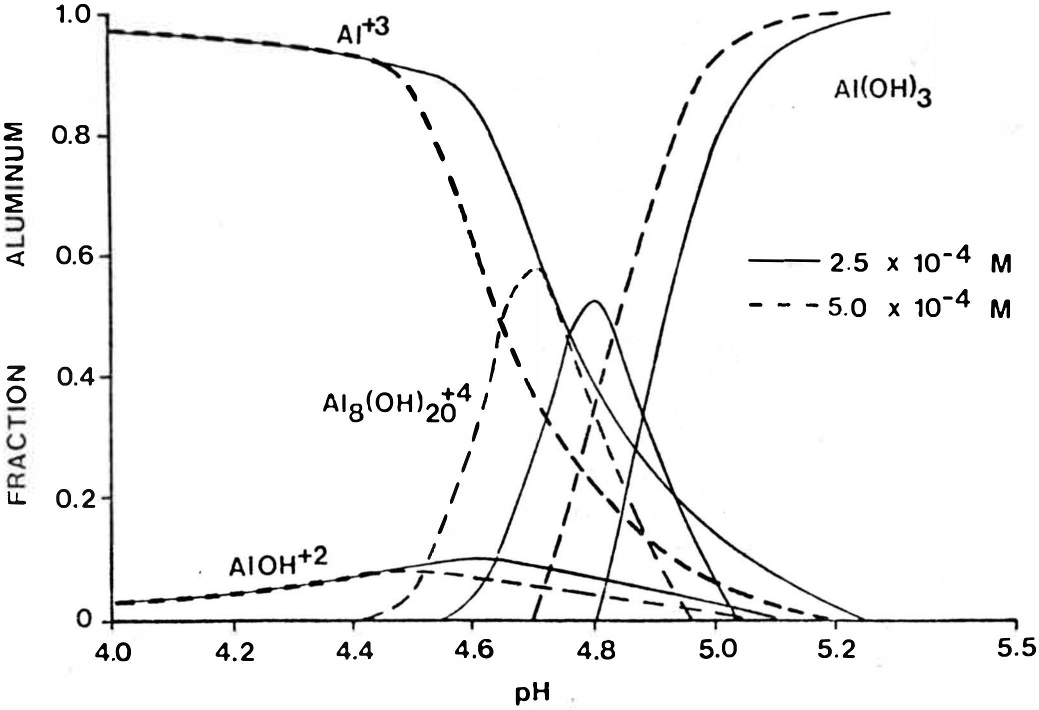


Figure 9. Distribution of Aluminum Species as a Function of pH and Aluminum Concentration at pH 4.0-5.5

description of the aqueous equilibria for aluminum sulfate could not be accurately determined by Hayden and Rubin.

Hayden and Rubin were able to determine the effect of the sulfate ion on the pHp. At these low aluminum concentrations, the sulfate ion decreased the pHp by .25 to .43 pH units. These results are shown in Table I.(7).

Table I. pHp for Aluminum at Different Concentrations.

Aluminum Concentration (M)	pHp $AlCl_3$	pHp $Al_2(SO_4)_3$
1.0×10^{-4}	4.90	4.65
5.0×10^{-4}	4.70	4.45
1.0×10^{-3}	4.68	4.25

Arnson studied aluminum adsorption on cellulosic fibers from dilute solutions of aluminum chloride and aluminum sulfate. Figure 10 shows how the initial rise in aluminum adsorption occurs as the polynuclear species begins to form for $AlCl_3$ (2). This increase in aluminum adsorption is shown at two different aluminum concentrations. The effects of increased aluminum concentration caused the adsorption curve to shift to a lower pH as did the distribution curve shown at the bottom of Fig. 10. The higher concentration also showed that more aluminum is being adsorbed onto the fibers.

Arnson's work also showed that adsorption behavior for aluminum ions of aluminum sulfate are analagous to those for aluminum chloride. Using Figure 11, a comparison of the two salts at the same concentration is shown (2). The observed differences between the two salts were that the aluminum sulfate

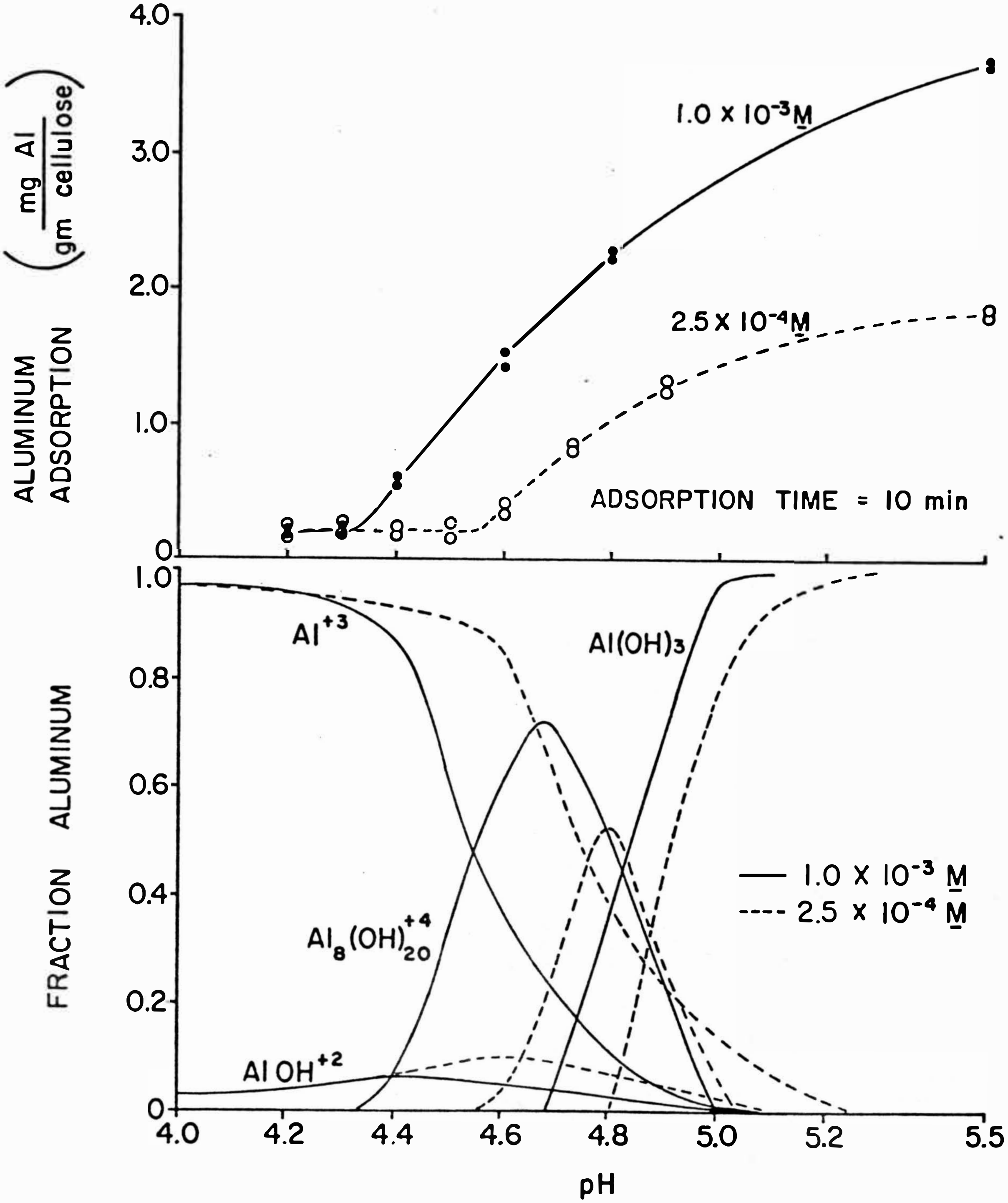


Figure 10. Top- Aluminum Adsorption as a Function of pH and Aluminum Concentration for $AlCl_3$. Bottom- Distribution of Aluminum Species as a Function of pH and Aluminum Concentration for $AlCl_3$.

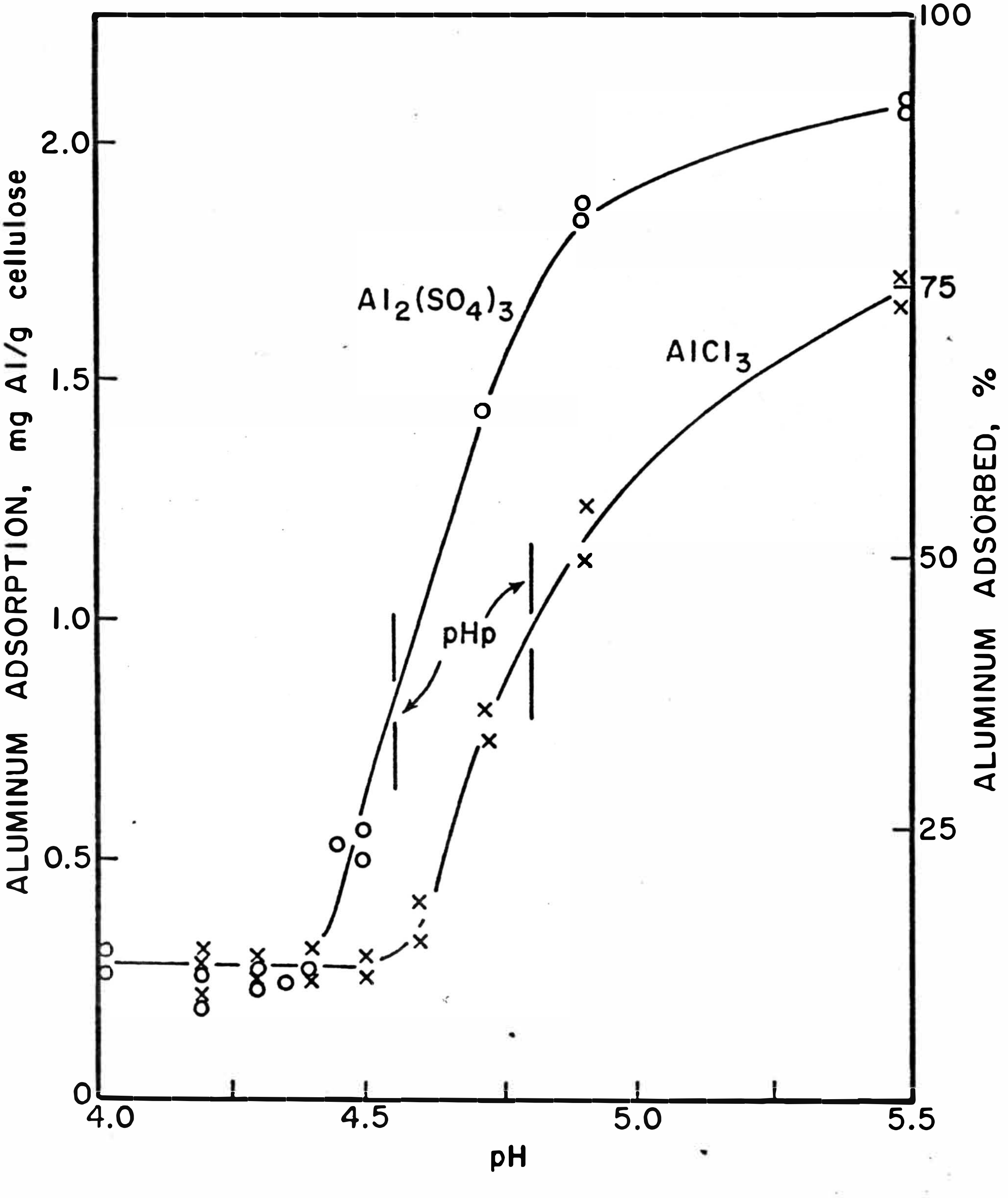


Figure 11. Comparison of Aluminum Adsorption for $AlCl_3$ and $Al_2(SO_4)_3$ ($2.5 \times 10^{-4}\underline{M}$). Solid Vertical Lines Denote the pH of Precipitate Formation (pHp) for each Aluminum Salt

adsorption curve broke upward at .25 to .30 pH units lower than for aluminum chloride. Also, the amount of adsorbed aluminum was greater for aluminum sulfate in the high pH range when the precipitate was formed. Arnson concluded the adsorption mechanisms of both aluminum sulfate and aluminum chloride were similar, although the exact formula of the polynuclear species for aluminum sulfate was not known.

Therefore, with an understanding of the aluminum aqueous equilibria, scientists can control and predict the interactions of aluminum species with other additives in the papermaking system. Since aluminum's interactions are controlled by its aqueous chemistry, it is necessary to control the pH and aluminum concentration before predicting how it will behave with other materials in the papermaking system.

ROSIN-ALUMINUM SIZING COMPLEX

Since paper is normally sized internally and the handsheets in this thesis will be sized with rosin, an overview of the effect of the rosin-aluminum sizing complex will be given.

Internal sizing of paper and paperboard is done to prevent penetration of aqueous liquids into the sheet. Rosin sizing is the typical internal sizing system. Guide (3,4,8) showed that to obtain good rosin sizing, three requirements must be met: 1) formation of low free-surface energy precipitates (thus, a high contact angle); 2) deposition of these precipitates onto the fibers; and 3) conversion of the wet size precipitate on the fiber surface to a stable low free-surface energy. The conversion aspect begins in the dryer section. Here the precipitate melts and flows over the surface of the fiber. The aluminum cations then anchor the rosin acid precipitates. This anchoring causes the hydrophobic portion of the molecule to be oriented outward from the fiber; thus, imparting sizing to the sheet.

The usual sizing procedure is to add the rosin size to the pulp and allow for adequate mixing before adding the aluminum sulfate, The rosin size and alum react to form the size precipitate. Also acids, acid salts, or the salts of alkaline earth metals can be used for precipitating rosin size, but none work as well as alum.

The theoretical amount of alum required to react with rosin size is about .37 parts of alum per one part of rosin size (9). In actual mill practice, about 1.5 to 2.0 parts of alum per part of rosin size are needed to obtain good sizing (9).

COMPOSITION OF THE SIZE PRECIPITATE

An obvious role of alum in sizing is to precipitate the rosin size, but considerable controversy has arisen over the nature of the rosin size precipitate. Jayme and Seidel (10) concluded that the size precipitate was made up of aluminum monoresinate, aluminum diresinate, and free acids. Back and Steenberg (11) showed that the size precipitate was an equimolar mixture of aluminum diabietate and abietic acid. Abietic acid is the principle rosin acid. Guide (3,4) studied size precipitates containing both sodium aluminate and sodium abietate. Guide's work showed that none of the products were stoichometric compounds, but instead coprecipitates of several compounds. Free abietic acid was found in all precipitates. The compositions of the size precipitate were independent of the pH of precipitation, but dependent upon the initial abietate-to-aluminum ratio prior to acidification. Davison (1) used aluminum sulfate to precipitate fully saponified rosin and analyzed the composition as aluminum diresinate and free rosin acids in slightly more than an equimolecular proportion along with a lesser amount of neutral rosin components.

When the pH increases in a papermaking system, the aluminum ions precipitate out of solution as aluminum hydroxide. Many believed that the aluminum hydroxide had no useful purpose in the size precipitate while Guide (4) thought the hydroxide olated with aluminum basic abietates to anchor and orient rosin molecules on cellulose fibers. This lead to his three requirements to obtain good sizing which were stated earlier.

Therefore, aluminum plays a key role in obtaining a precipitate by securing the rosin size to the cellulose. There is still much controversy in this area of precipitate composition, but the aluminum role has been agreed upon to be of importance in the mechanism of sizing. Brannstrom's thesis (14) used reverse sizing and showed that aluminum adsorption onto fibers before size addition, tied up the aluminum ion and reduced its ability to precipitate the rosin size onto the fibers. Therefore, the greatest sizing occurred where the aluminum adsorption was lowest.

ROLE OF POLYACRYLAMIDE IN ROSIN-ALUM SYSTEM

In the late 1950's, a modified acrylamide polymer was developed as a pulp additive for improving the dry strength. Polyacrylamide in the presence of alum and rosin size has been found to increase the dry tensile, burst, and fold while also increasing the sizing response without changing the desirable sheet properties. Polyacrylamides have also been used as a retention aid to increase the amount of filler or fines in a sheet.

With the addition of polyacrylamide to a rosin-alum system, Reynolds (12,13) showed that a larger amount of alum is needed in the system. Figure 12 shows that by increasing the amount of alum added to the polyacrylamide system will show an increase in dry strength properties. This work was completed before a more comprehensive understanding of aluminum chemistry fundamentals had been completed by Hayden, Rubin, and Arnson.

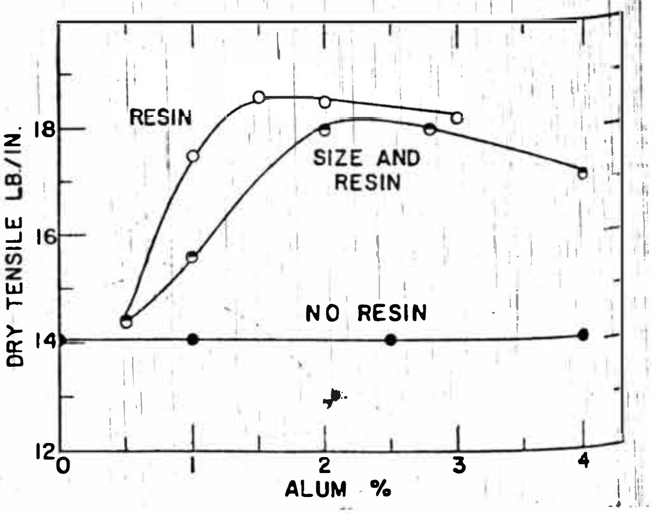


Fig. 12. Alum usage versus Efficiency of Resin Treatment.

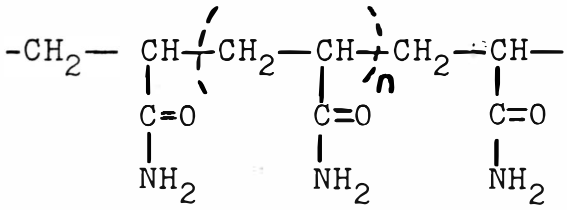
The principle factors which determine the dry strength of the paper are: 1) strength of the fiber itself, 2) strength of the fiber to fiber bond, 3) number of fiber to fiber bonds, and 4) formation of the sheet. The generalized theory of how polyacrylamides affect dry strength is that the beater additive can not affect the strength of the fiber itself; therefore, it is the bonds between the fibers which the polyacrylamide affects and determines the dry strength.

Polyacrylamides are linear, anionic polymers which bond well to cellulose. The mechanism which involves depositing the resin on the pulp to develop improved strength is still being investigated. The resin may deposit on the fibers as an aluminum resinate or a resin molecule may react directly with an aluminum ion already attached to the cellulose fibers. Through electron micrographs other physical measurements, Reynolds, Linke, Landes, et al have postulated that the polyacrylamide resin bridges between fibers that are too far apart for hydrogen bonding to occur and thus impart dry strength properties to the sheet.

Reynolds, Linke, and others (12,13,17, 18) showed that the stock pH is an important variable in rosin size-polyacrylamide pulp slurries. Their work concluded that a pH between 4.2 and 5.0 gave the maximum effectiveness of the dry strength resin. Control of pH in the system is essential for retention of polyacrylamide by cellulose fibers. If the pH is too high, $Al(OH)_3$ is formed; and although it can be retained by the pulp, the precipitate does not form a salt which is necessary to fix the polymer to the fibers with the carboxyl groups of the resin.

Since pure polyacrylamide is not retained in the pulp, it appears that resin retention is possible by the metal ions, aluminum for instance, reacting with the carboxyl groups of the resin.

Reynolds also examined the order of addition of polyacrlamides before and after adding alum and rosin size. The greatest dry strength improvement occurred when polyacrylamide was added after the rosin and alum. Reynolds was trying to locate the optimum wet end application point for the resin to give maximum dry strength properties. Once again, polyacrylamide research scientists concluded that it is the aluminum chemistry which affects the degree of retention of both the rosin size and polyacrylamide to the fibers.



$$-CH_2-\underset{\substack{|\\C=O\\|\\NH_2}}{CH}-\left[CH_2-\underset{\substack{|\\C=O\\|\\NH_2}}{CH}\right]_n-CH_2-\underset{\substack{|\\C=O\\|\\NH_2}}{CH}-$$

Molecular formula of Polyacrylamide where n= 1000 to 100,000 acrylamide units.

LAB PROCEDURE

A handsheet making procedure was used to accomplish the objectives of this thesis. This procedure was standardized before beginning the actual thesis work. A pulp blend of 50% bleached hardwood/ 50% bleached softwood was refined in the Valley Beater to a freeness of 400 ml CSF. The British handsheet tower was used in forming the sheets.

In the handsheet standardization process, 50 handsheets of .6% consistency (3.6 grams o.d. fiber) were made by: 1) obtaining a 260 cc pulp sample; 2) adjusting the pH with .2M HCl to 4.1-4.4 pH; 3) adding 10 ml of 13.5 ppm aluminum species as $AlCl_3$; 4) raising the pH to 4.1-4.4 with .25M NaOH; 5) adding rosin size at .75% based on oven dry fiber; and 6)adding the polyacrylamide (Accostrength 86) at .50% based on oven dry fiber. The handsheet was constantly agitated during this procedure using a magnetic stirrer-mixer. The tower pH was adjusted with HCl to 4.5. The handsheets were pressed for five minutes on one side and then turned over for an additional two and a half minutes at 50 psi in the British sheet mold press. The handsheets were then dried on the cylinder dryer at 220°F using two passes. Pressing and drying variables had to be kept constant. If not, the apparent density and the relative bonding area would change and thereby cause differing values in dry strength properties that are not due to the level of polyacrylamide added. All handsheets were conditioned overnight in the

50% RH, 72^{O}F room before testing. Initially, handsheets were tested for Scott Bond, burst, tensile, tear, TEA, and sizing using the Hercules Size Tester. Sizing tests were dropped after this standardization procedure because not enough handsheets would be made in future trials to obtain accurate, reproducible results.

Four major steps can broadly begin to cover the topic of aluminum chemistry and order of addition as related to dry strength properties. The first three steps- varying the aluminum concentration and pH, varying the level of polyacrylamide added, and changing the order of addition were accomplished in this thesis. The fourth step, the relationship of refining to dry strength properties was not done due to time constraints.

After the fifty handsheet standardization procedure was completed, only thirty handsheets were made in each future trial.

The first major area of concern varied the pH of the stock between 4.0 and 5.0 to obtain different aluminum species. This was accomplished by lowering and then readjusting the pH when the aluminum as $AlCl_3$ was added. Three aluminum concentrations that are typical for industry were used in this step as seen in Table II (25).

Table II. pHp for Aluminum at Different Concentrations Used.

Aluminum Concentration (M)	ppm	pHp ($AlCl_3$)
1.0×10^{-3}	27	4.65
2.5×10^{-4}	6.8	4.80
5.0×10^{-4}	13.5	4.70

Using 27 ppm aluminum concentration as an example, three handsheet sets or 90 handsheets were made at this concentration-thirty handsheets at a pH below 4.65 to obtain the aluminum trivalent cation, thirty handsheets at a pH of 4.65 to obtain the polynuclear species, and thirty handsheets at a pH greater than 4.65 to obtain the aluminum precipitate. These handsheets were made by the procedure described previously. In this first step, 270 handsheets were made varying the pH to achieve different aluminum species using different aluminum concentrations of $AlCl_3$ while keeping the rosin size and polyacrylamide levels constant. From the results of these handsheets, a "best" aluminum concentration and pH range was chosen to complete this thesis.

Using this "best" aluminum concentration and pH as judged by the dry strength results of the first step, five sets of handsheets were made changing the level of polyacrylamide between 0 and 1.2 % based on oven dry fiber. Again the same basic handsheet procedure, pressing, and drying were used. The rosin size level remained at .75% based on o.d. fiber as in the first step. Handsheets were again tested for Scott Bond, burst, tensile, tear, and TEA.

The third area of concern was to adjust the order of addition using the aluminum concentration, pH, and polyacrylamide level chosen from the first two parts of this thesis. Four handsheet trials were made in this step. Polyacrylamide was added first to the pulp, added between the rosin and aluminum in another trial, and added last in two trials which varied the order of addition of aluminum and rosin size. These results would give an indication of whether the order of addition in a paper mill makes a signigicant difference in the dry strength values. The results of these handsheets would only give an indication of the relationship between order of addition and dry strength properties since the time aspect for retention was not being taken into account.

DISCUSSION OF RESULTS

Varying the Aluminum Concentration and pH of the system

When studying the effects of different aluminum species as related to dry strength variables, it is important to specify the pH and aluminum concentration of the system. At the aluminum concentrations and pH ranges which were chosen for these experiments, Hayden and Rubin had analyzed the aluminum species distribution. This distribution curve, Figure 8, shows which aluminum species exist in solution between the pH range of 4.0 to 5.5. As discussed earlier, the pH range can be broken up into three areas: 1) the low pH range where the Al^{3+} ion predominates, 2) the intermediate pH range where the polynuclear species reaches its maximum concentration, and 3) the high pH range where the aluminum precipitates out of solution as $Al(OH)_3$.

Previous work measured the pH where precipitation of $Al(OH)_3$ begins (pHp) in both aluminum chloride and aluminum sulfate systems. In the aluminum chloride system , this pHp coincides with the same point at which the polynuclear species reaches its maximum concentration.

In this experiment, three aluminum concentrations and three pH ranges as explained with Table II, were used in determining if one aluminum concentration and pH range would lead to higher dry strength values than the other concentrations and pH's. Table III shows the results of varying only the pH range at a specified aluminum concentration to obtain the different aluminum species. The aluminum concentration which lead to the highest strength properties was in the pH range which gives the maximum concentration of polynuclear species as seen in Table III. The higher strength values obtained at the pHp are due to Arnson's work that the initial rise in aluminum adsorption occurs as the polynuclear species begins to form for $AlCl_3$; and with this rise in adsorption, there are more possible interaction sites to "fix" the polyacrylamide onto the fibers. Reynolds (12,13) showed that by increasing the amount of alum added to the polyacrylamide system, there would be an increase in dry strength porperties. This idea can be transferred to an aluminum chloride system because it is a similar system, but less complicated than the alum system due to no sulfate ion being present in the system to cause complexing.

Table III. Results of varying aluminum concentration and pH.

Concentration (ppm)	pH	Tear (g)	Burst (psi)	Scott Bond (ft-lb)	Tensile (kg/15mm)
13.5	4.1	402	153	168	17.42
13.5	4.65	456	169	160	18.03
13.5	5.0	515	167	151	17.68
6.8	4.1	406	159	184	15.50
6.8	4.8	387	185	218	18.50
6.8	5.0	412	180	224	16.12
27	4.1	510	163	120	17.15
27	4.7	385	157	152	17.44
27	5.0	387	174	220	16.95

The smallest aluminum concentration used, 2.5×10^{-4}, was chosen to complete this thesis. Figures 13 and 14 clearly indicate that the 2.5×10^{-4} concentration at any pH value, but especially its pHp of 4.8 gave the best Scott Bond and bursting strength results. In Figure 16, the peak tensile value also occurred at the pHp of 2.5×10^{-4}M (6.8 ppm) aluminum concentration. Tear should not be effected by polyacrylamide in the sheet. Tear is related more to fiber length than to fiber-to-fiber bonding which is what the polyacrylamide affects in the sheet. Therefore, the results of Figure 15 further verify that the concentration of 6.8 ppm is the ideal concentration to use in further work.

Once again, to summarize the results of the first area of this thesis, further experiments used an aluminum concentration of 2.5×10^{-4} and at a pH of 4.8 (its pHp). This concentration and pH gave the best overall dry strength results. The reasoning behind choosing this aluminum concentration and pH was that at the pHp, the maximum aluminum concentration is being adsorbed onto the fibers. Therefore, with more aluminum present in the system, there are more possible interaction sites to "fix" the polyacrylamide between the fibers,which are at greater distances than possible for hydrogen bonding to occur, using the aluminum precipitate as the anchoring medium; and thereby increase the dry strength properties of the sheet.

Varying the Level of Polyacrylamide in the System

In the second step of this tesis, the level of polyacrylamide was varied between 0 and 1.2% based on o.d. fiber. The results are shown in Table IV and Figures 17-20. Dry strength

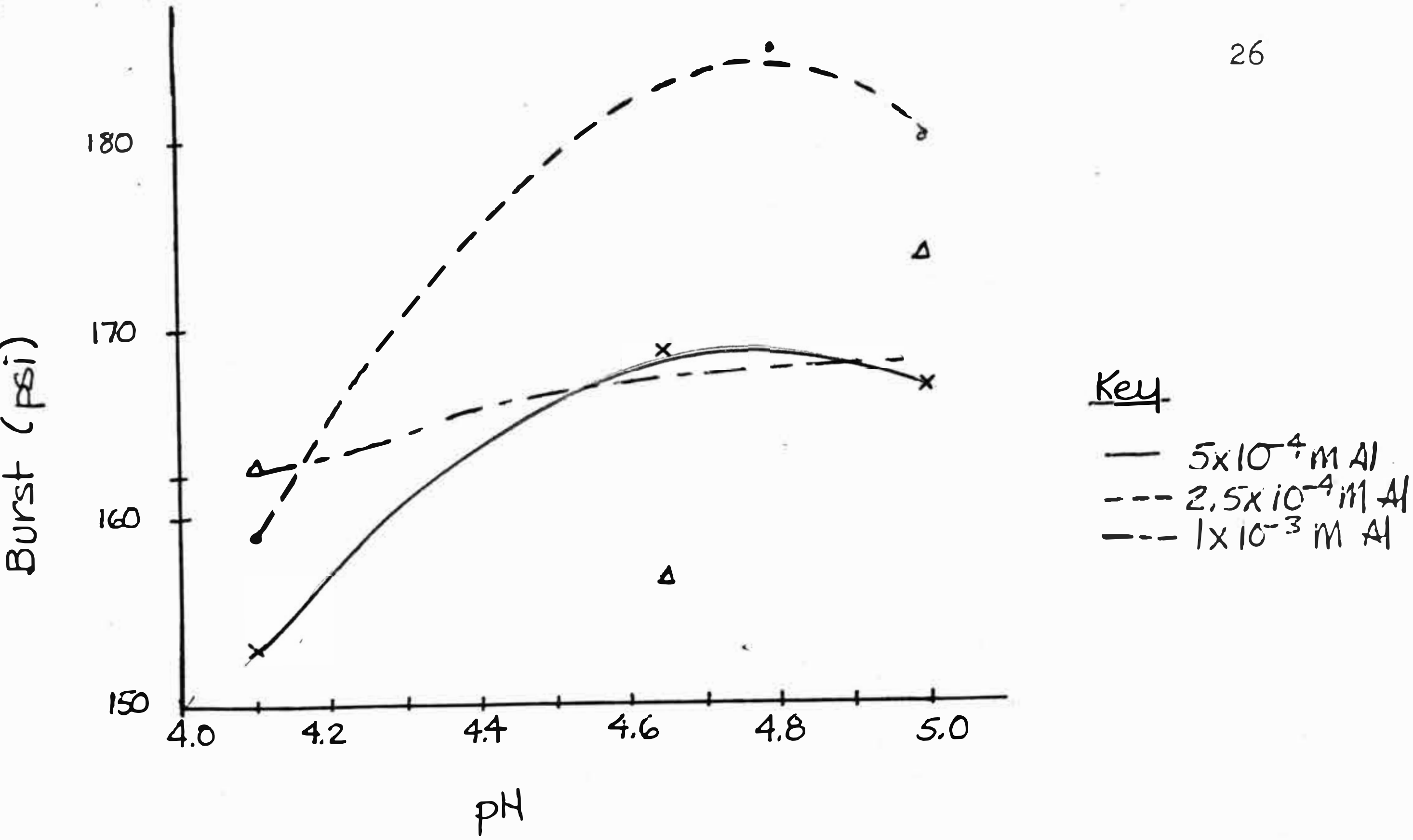


Figure 13. The Effect of pH on Burst

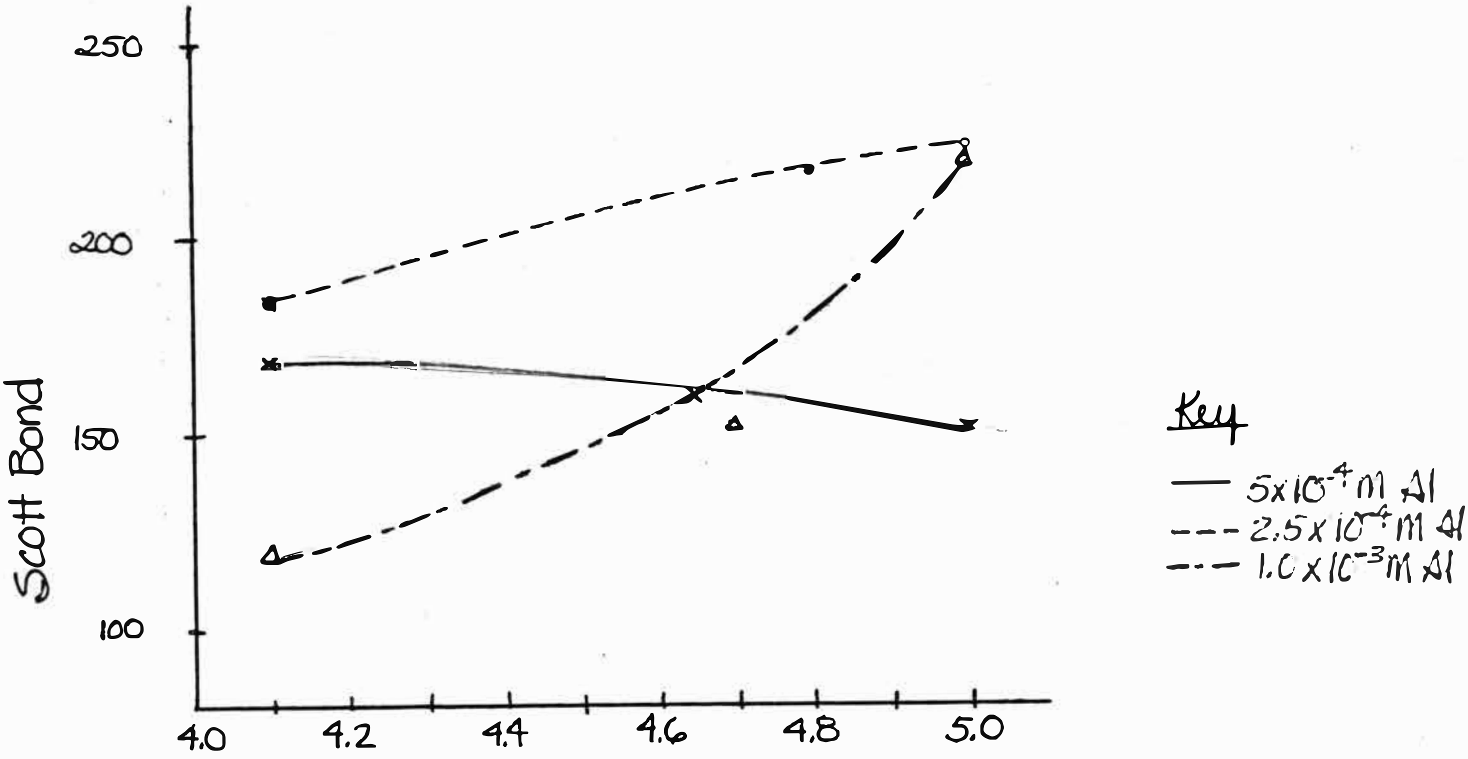


Figure 14. The Effect of pH on Scott Bond

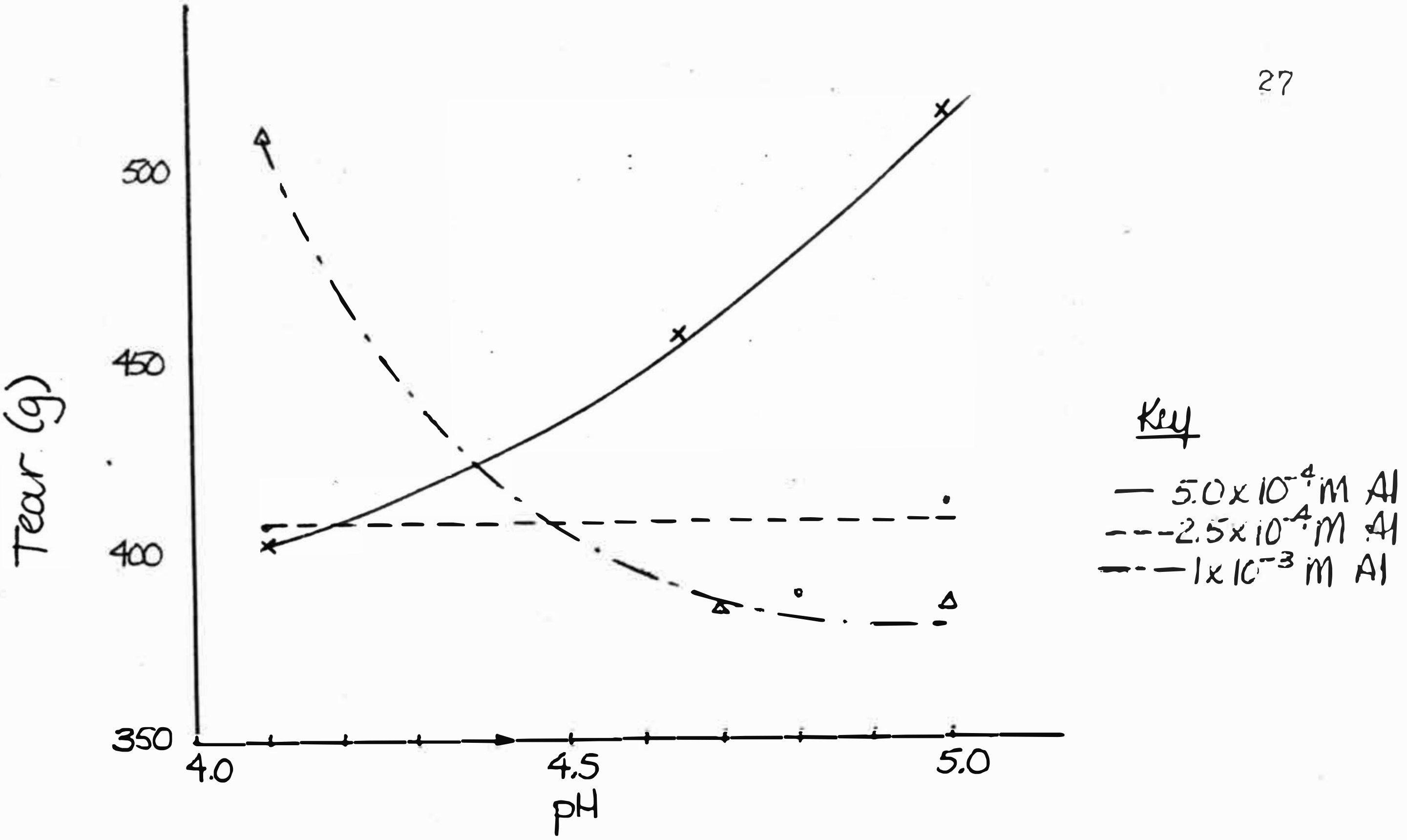


Fig. 15. The Effect of pH on Tear

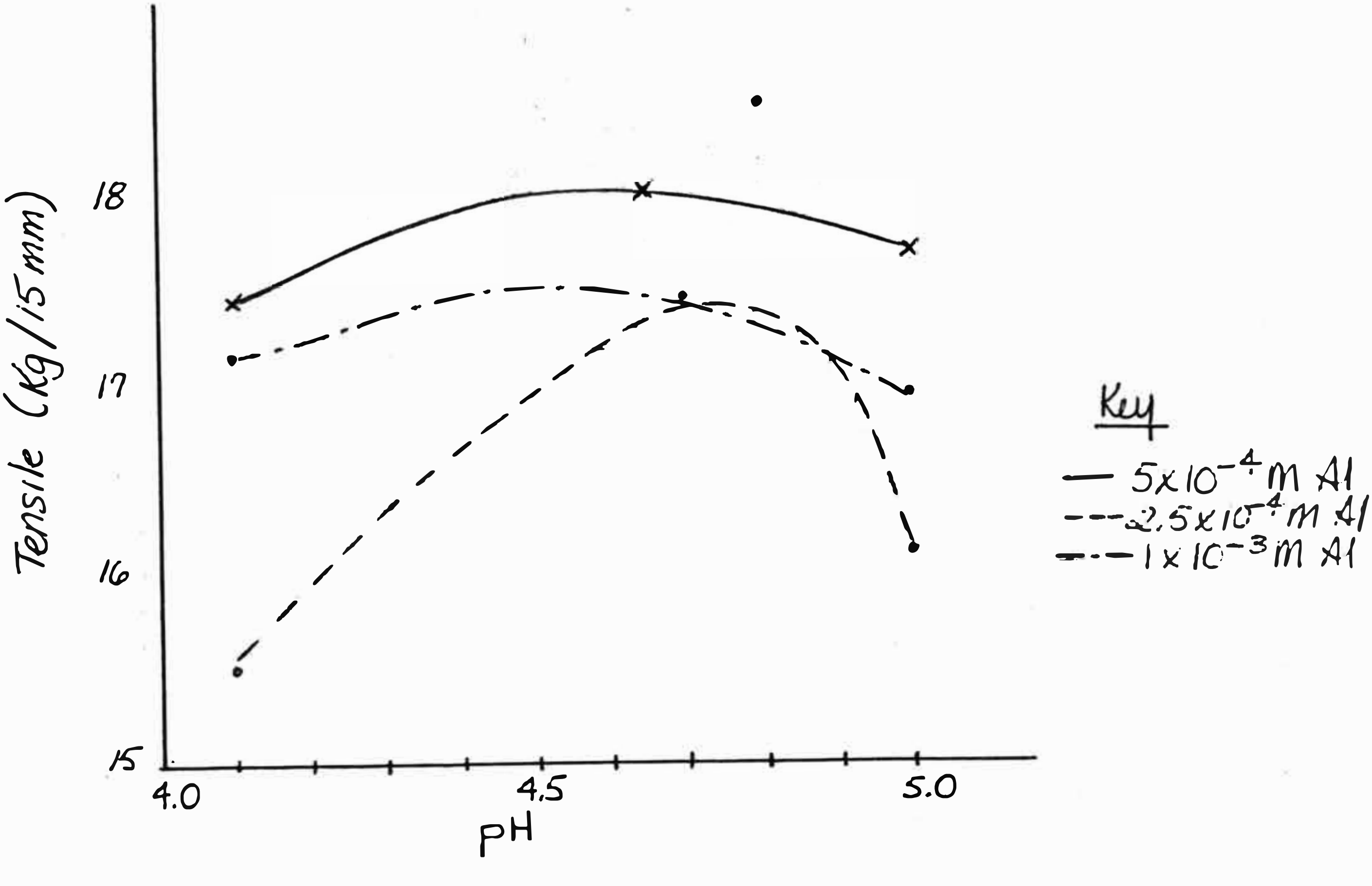


Fig. 16. The Effect of pH on Tensile

Table IV. Dry Strength Results using 6.8 ppm at a pH of 4.8.

PAA$^-$ (%)	Burst (psi)	Tear (g)	Scott Bond (ft-lb)	Tensile (kg/15mm)
0	157	426	211	14.31
.3	162	392	216	16.10
.5	163	420	226	15.35
.7	172	408	222	17.00
.9	161	422	231	16.12
1.1	160	398	240	14.60

values peaked and began to level off once a concentration of .5-.7% resin was added to the pulp. In literature cited (12,13), the polyacrylamide resin efficiency curve began to flatten out at different levels depending on the type of pulp used, the amount of refining, and the presence of fillers in the sheet. The .5% resin level was chosen as the polyacrylamide concentration to use in completing this thesis. The reasons for choosing this concentration are evident from burst and tensile responses as seen in Figures 18 and 20.

Scott Bond values continually increased as the level of polyacrylamide increased in the sheet. This result, shown in Figure 17, was expected. With more polyacrylamide in the sheet, one would expect stronger fiber-to-fiber bonding (higher Scott Bond values) due to more bonding gaps being filled with the dry strength resin. Scott Bond is considered to be the strength test which comes closest to measuring the true fiber-to-fiber bonding strength of paper. The results of Figure 17 would lead one to believe that by the continual addition of large levels of polyacrylamide, outstanding dry strength values are attainable.

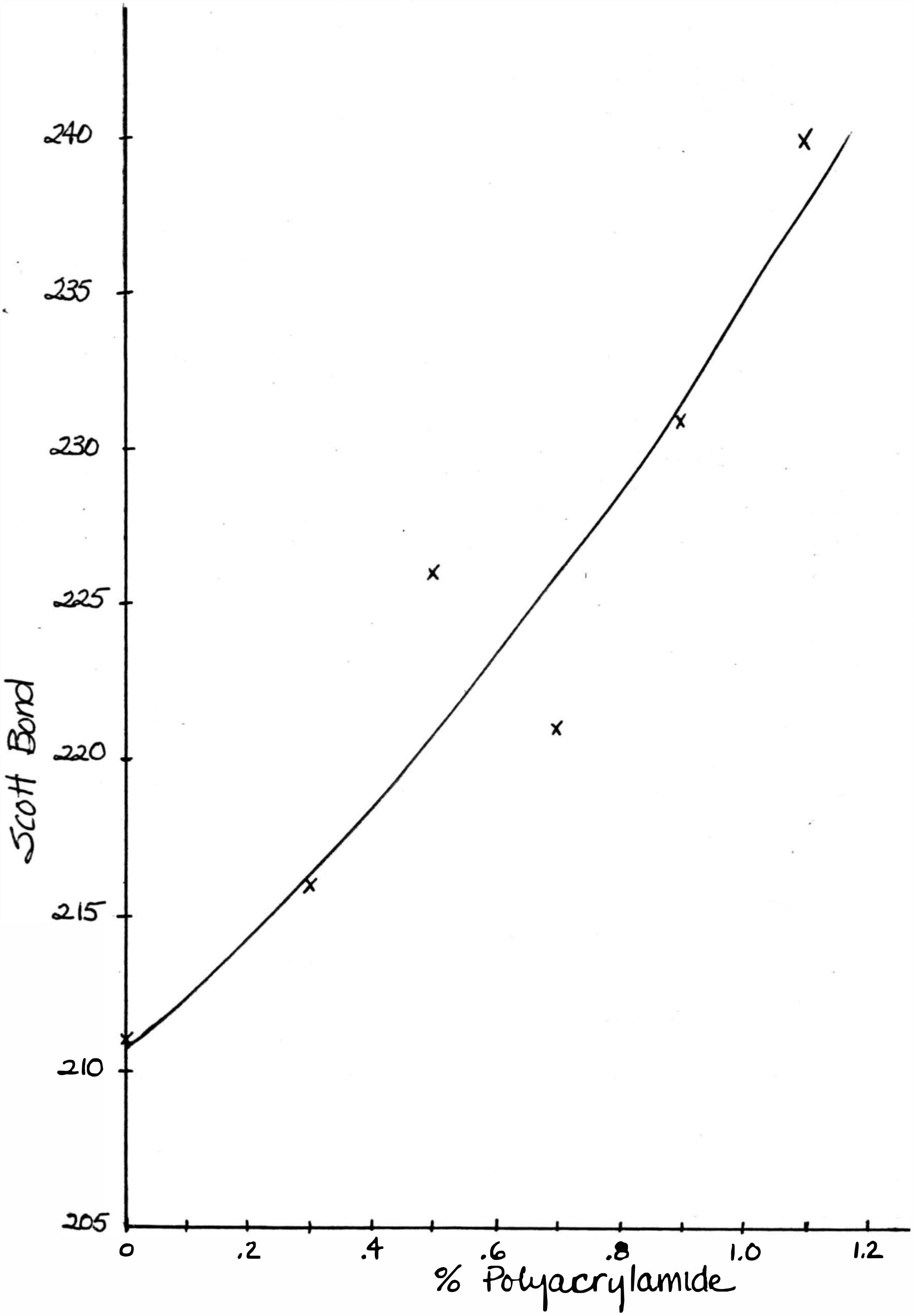


Fig 17. Effect of % Polyacrylamide on Scott Bond

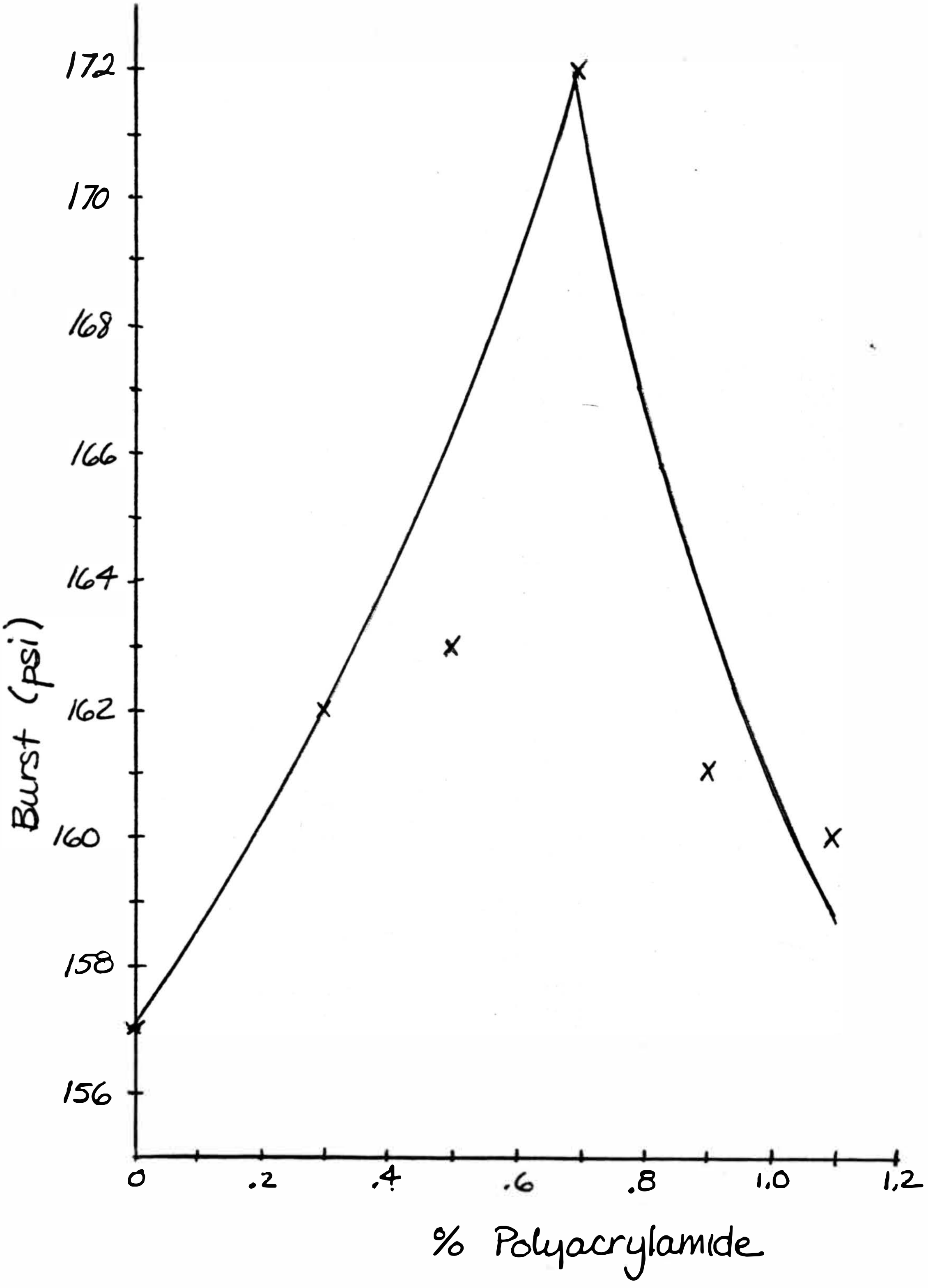


Fig. 18 Effect of % Polyacrylamide on Burst

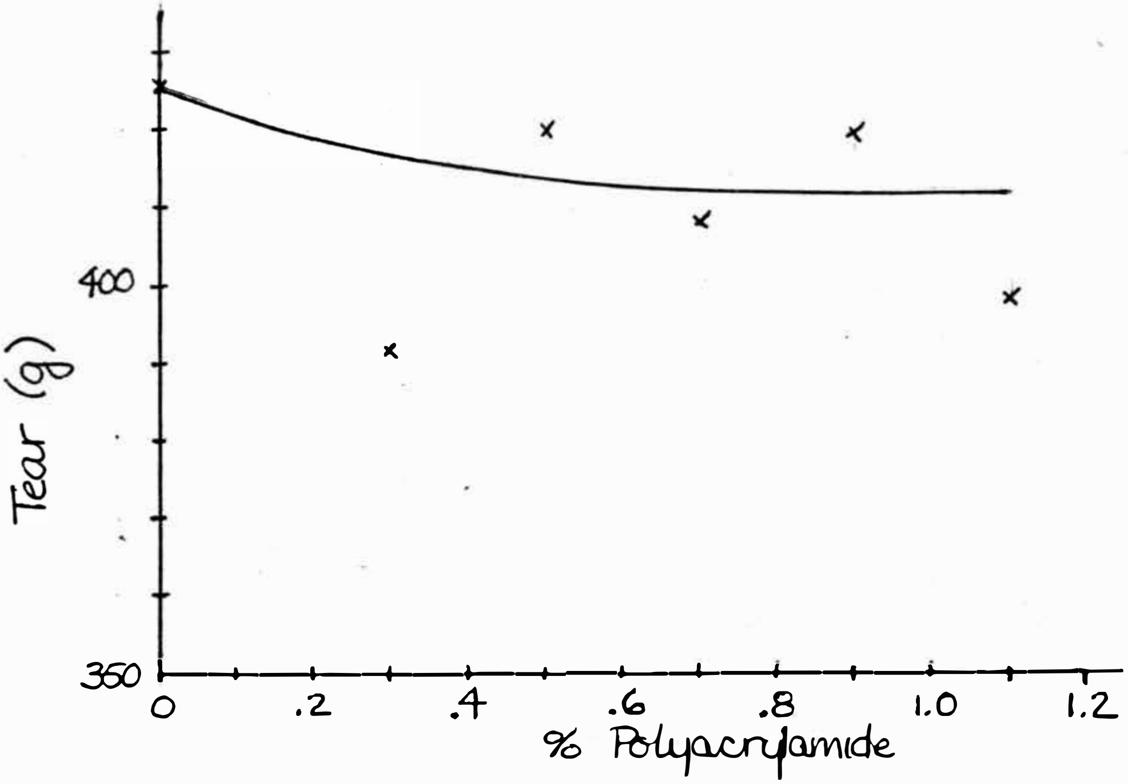


Fig 19 Effect of % Polyacrylamide on Tear

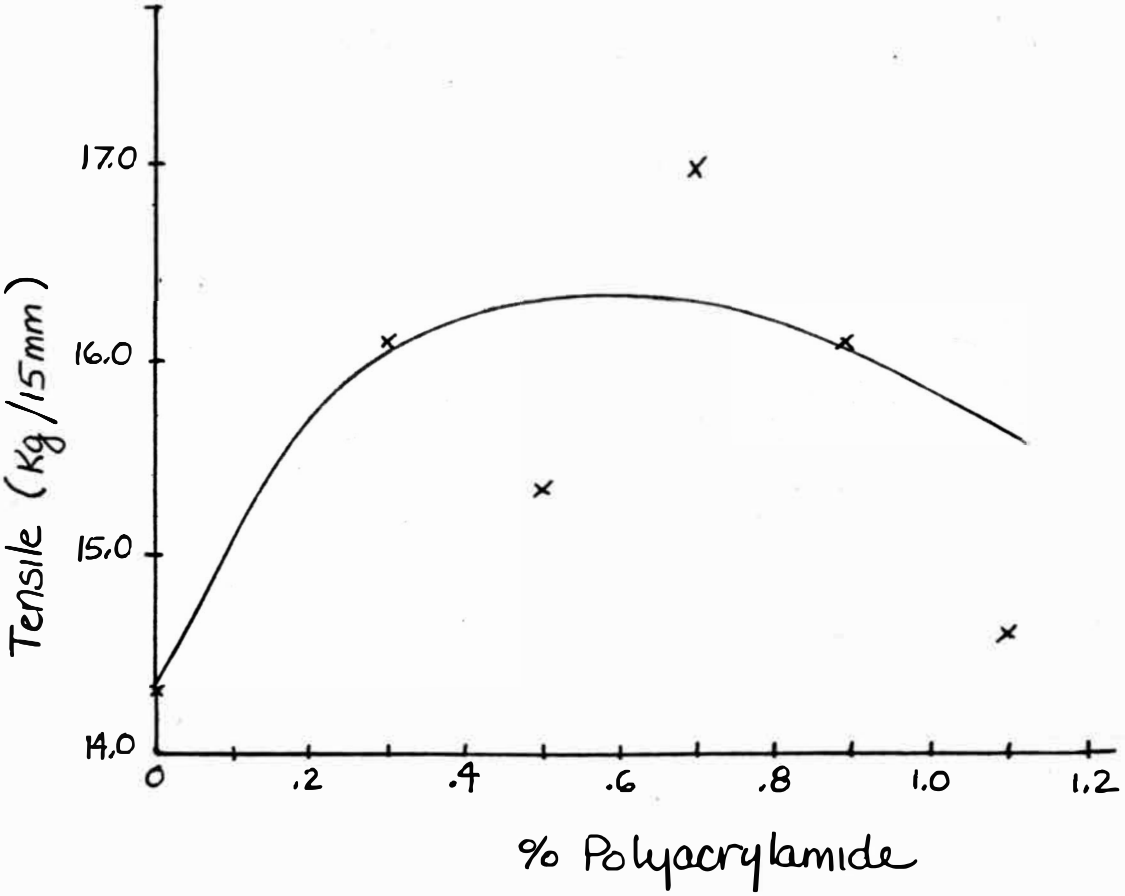


Fig 20. Effect of % Polyacrylamide on Tensile.

For a mill to remain competitive in costs, the best overall dry strength value was used rather than just choosing a resin level which gave the highest Scott Bond data. There is no need to use 1.0% resin to achieve dry strength specifications if .5% or .7% resin could obtain a similar dry strength value; and thus save on the cost of materials.

In summary, a polyacrylamide level of .5% based on o.d. fiber was used in completing this thesis. This resin level was chosen because .5% resin was at the beginning of the peak and leveling off of dry strength values as seen in Figures 18 and 20. Once again, tear values are not affected by the polyacrylamide concentration as shown in Figure 19. Scott Bond values continually increased as the concentration of polyacrylamide increased in the sheet. Therefore, the .5% resin concentration was used because this level gave the best overall dry strength responses.

Varying the Order of Addition

The third area and main objective of this thesis employed the results of the first and second areas involving aluminum concentration, pH, and polyacrylamide concentration. This area focused on whether or not the order of addition of polyacrylamide, aluminum species, and rosin size is essential in obtaining improved dry strength responses.

Handsheets with an aluminum concentration of 6.8 ppm and at a pH of 4.8 with a resin level of .5% based on dry fiber were used in varying the order of addition. The rosin size level remained at .75% based on dry fiber. Four trials were made: 1) polyacrylamide, rosin, aluminum (PRA, for short), 2) rosin, aluminum, polyacrylamide (RAP), 3) aluminum, rosin, and polyacrylamide

(ARP), and 4) rosin, polyacrylamide, and aluminum (RPA).

The results of varying the order of addition imply that there is virtually no signigicant difference in dry strength responses other than those due to statistical variance as seen in Table V. The order of RPA gave slightly better dry strength responses than the other orders of addition.

Table V. Varying the order of addition.

Order of Addition	Burst (psi)	Tear (g)	Scott Bond (ft-lb)	Tensile (kg/15mm)
PRA	164	414	213	14.19
RAP	182	405	202	14.12
ARP	166	403	208	15.94
RPA	182	425	221	13.12

The RPA order appeared to give the best overall strength results. RPA had three of the four highest strength properties with only tensile values at the low end of the spectrum. This result of RPA's order in obtaining slightly better strength responses than the other orders of addition is interesting since previous work by Reynolds indicated otherwise (12,13). Reynold's work showed that both rosin and alum must be added before the polyacrylamide to the system to achieve the greatest dry strength improvement. Reynold's work was completed before a better understanding of aluminum chemistry had been investigated by Hayden, Rubin, and Arnson, et al.

The results shown in Table V lead to the hypothesis that the aluminum does not have to be present to fix the polyacrylamide in between the fiber bonds. Retention time and the amount of polyacrlyamide retention are key variables which affect the dry strength response. These variables were not taken into account during this study. Another factor which must be taken into account is the degree of mixing after each chemical. With the RPA system, the pulp was mixed for two minutes after the aluminum was added so that the aluminum species would have time to secure the resin to the cellulose. With RAP and ARP orders of addition, once the polyacrylamide was added to the system, the mixer was turned off in a matter of seconds and the handsheet was formed. This could account for the differences in dry strength values between RPA and the others.

In reviewing these results, RAP, PRA, and ARP are virtually indistinguishable in overall dry strength results once the RPA order of addition is chosen to give the best overall dry strength properties. This would seem to indicate that in a mill situation, there could possibly be no advantage to adding one chemical prior to another as long as the aluminum is allowed time within the system to secure the resin to the cellulose.

Also note that the point of resin addition was after refining; in many mills, alum and rosin size are added before refining while the dry strength resin is added afterwards. If the alum and resin are both added before refining, the effectiveness of the resin in the system has been shown to be proportional to the amount of refining. A refining study which varied the orders of addition with this newer understanding of the aluminum chemistry would shed more light on this area of concern.

CONCLUSIONS AND RECOMMENDATIONS

Greater improvements in dry strength values can be obtained by maintaining the system's pH at the pHp as shown in the first area of this work. By using the pHp as the system's pH, more aluminum can be adsorbed onto the fibers. With more aluminum adsorbed onto the fibers, there are more possible interaction sites for the polyacrylamide to be "fixed" between the fibers; and thereby give a higher dry strength response.

The optimum level of polyacrylamide, .5%, for this experiment was determined in the second part of this thesis. Polyacrylamide's dry strength effectiveness is dependent on the type of pulp used, the degree of refining, and the amount of filler or fines in the sheet. Tensile and burst values increased and then leveled off once a concentration of .5-.6% resin was added to the sheet. Scott Bond values continually increased as the level of resin increased in the sheet due to the sheet's stronger fiber to fiber bonds with more polyacrylamide present in the system.

There was virtually no signigicant difference in dry strength results when varying the order of addition. Reasons for these interesting results are not apparent. This would seem to indicate that in a mill situation, there would be no advantage in adding one chemical before another as long as there would be sufficient time for the aluminum to secure the polyacrylamide to the cellulose.

Further work investigating the effects of refining on the order of addition of a rosin, aluminum, and polyacrylamide system could be a future thesis. A WMU pilot machine trial would give more credibility to this subject. A pilot machine trial would also take into account the retention times of the chemicals; and, lead to an even better understanding of the impact of aluminum chemistry and order of addition on anionic dry strength resins,

LITERATURE CITED

1. Davison, R.W., Tappi 47(10), Oct. 1964.
2. Arnson, T.R.,"The Adsorption of Complex Aluminum Species by Cellulosic Fibers", Doctoral Dissertation, Institute of Paper Chemistry, 1980.
3. Guide, R.G., Tappi 42(9):734 (Sept. 1959).
4. Guide, R.G., Tappi 42(9):740 (Sept. 1959).
5. Price, D., Paper Trade Journal 126(15), April 8, 1948.
6. Bronsted, J.N., and Volquartz, K.Z., Journal of Physical Chemistry 134:97 (1928).
7. Hayden, P.L., and Rubin, A.J., "Systematic Investigation of the Hydrolysis and Precipitation of Aluminum (III), in Rubin's Aqueous Environmental Chemistry of Metals", Ann Arbor, Ann Arbor Science, p. 317, 1974.
8. Cobb, R.M.K., and Swanson, J.W., Internal Sizing of Paper and Paperboard, Tappi Monograph Series No. 33, 1971, p. 3.
9. Casey, J.P., Pulp and Paper, Volume 1, New York, Interscience Publisher, 1952, p. 490.
10. Jayme, G., and Seidel, W., Das Papier, 11:500 (1957).
11. Back, E., and Steenberg, B., Svensk Papperstidn, 54(15) 510 Aug. 15, 1951.
12. Reynolds, W.F., and Linke, W.F., Tappi 46(7), July 1963.
13. Reynolds, W.F., Tappi 40(10):839 (Oct. 1957).
14. Brannstrom, K., Senior Thesis, 1981, Western Michigan Univ.
15. Moore, E.E., Tappi 59(6):120 (June 1976)
16. Reynolds, W.F., Tappi 57(3):116 (March 1974).
17. Linke, W.F., Tappi 45(4):326 (April 1962).
18. Linke, W.F., Tappi 51(11):59A (Nov. 1968).
19. Swanson, J.W., Tappi 39(5):257 (May 1956).
20. Chan,L.L., Pulp and Paper Canada, 77(6), June 1976.
21. Strazdins, E., Tappi 48(3):157 (March 1965).

22. Davison, R.W., Tappi 58(3):48 (March 1975).

23. Strazdins, E., Tappi 64(1):31 (Jan. 1981).

24. Kulick, R.J., Tappi 60(10):74 (Oct. 1977).

25. Arnson, T.R.,"The Chemistry of Aluminum Salts in Papermaking", Institute of Paper Chemistry, 1980.

DRY STRENGTH OF PAPER

1. Aitken, T.; Anderson, D. R.; Jursich, M. J.; Nalco Chemical Co. Cationization of starch for filler retention utilizing a cationic polyepihalohydrin-tertiary amine polymer. U.S. pat. 3,674,725(July 4, 1972); ABIPC 43:A6757.

Starch is reacted under alkaline conditions with a polymer formed from polyepichlorohydrin and an amine such as trimethylamine. The product is of use in paper manufacture as a retention and drainage aid, and as a strength-improving agent.

2. Aitken, T.; Nalco Chemical Co. Cationic starch and condensates for making the same. U.S. pat. 3,854,970(Dec. 17, 1974); CA 82:A87984.

Wet-end papermaking additives were prepared comprising the reaction product of alkali-treated starch with dimethylamine-epichlorohydrin reaction products or ammonia-dimethylamine-epichlorohydrin reaction products. The burst strength of paper was improved by incorporating the additives in pulp in the amount 10 lb/ton as pH 5.5.

3. Allgemeine Papier-Rundschau. Chemical products for addition to pulp. Allg. Papier-Rundschau (3):76-8, 80-2, 85-6, 88-91; (24/25):918, 920(Jan. 20, June 20, 1972); Ger.; ABIPC 43:A4877.

An alphabetical list is given of numerous trade-named pulp additives, showing the manufacturer (supplier), chemical nature, and recommended applications. Included are fillers, pigments, optical brighteners, sizing agents, dry and wet-strength agents, retention and drainage aids, preservatives, plasticizers, surfactants, lubricants, water and oil repellents, pitch control agents, etc.

4. Allgemeine Papier-Rundschau. Chemical products for beater addition [in papermaking]. Allg. Papier-Rundschau (1):8, 10, 15-18, 20-2, 24, 26, 28-30, 32-3 (Jan. 6, 1975); Ger.; ABIPC 45:A11931.

Over 200 chemicals (retention aids, dewatering accelerators, rotproofing agents, sizing agents, dry- and wet-strength agents, wetting agents, fillers, optical brighteners, pitch-control aids, etc.) are listed by trade name, manufacturer, chemical composition, and areas of application.

5. Allgemeine Papier-Rundschau. Chemical products of use as beater additives. Allg. Papier-Rundschau (1):18-32(Jan. 5, 1974); Ger.; ABIPC 45:A3757.

A list is presented of approximately 250 trade names referring to beater additives of use in papermaking (strength-improving agents, retention aids, dewatering accelerators, sizes, wetting agents, rosin-size precipitating and fixing agents, plasticizers, fillers, optical brighteners, pitch control agents, dyes, microbicides, defoamers, wet-strength agents, flocculating agents, etc.). The trade names are listed along with manufacturer, chemical composition, and applications and characteristics.

6. Allgemeine Papier-Rundschau. Chemical products suitable as pulp additives. Allg. Papier-Rundschau (3):90, 92-4, 96-8, 100-2(Jan. 20, 1971); Ger.; ABIPC 42: A5558.

This directory of trade-named compounds and formulations for use as special-purpose paper and pulp (wet-end, beater, etc.) additives lists their chemical composition (where known), supplier, special characteristics, and recommended applications. Included are dry- and wet-strength agents, flame-, water-, and fungus-proofing compounds, sizing and impregnating agents, surfactants, asphalt and pitch dispersants, foam inhibitors, pigments, fillers, dye fixatives, optical brighteners, retention and drainage aids, coagulants, plasticizers, etc.

7. Anchor Continental Inc. Impregnating a permeable polymeric material. Ger. Offen. pat. 2,264,699(Aug. 1, 1974); CA 81:A170786.

The dry and wet strength of NCO-reactive, permeable substrates, such as paper, is improved by impregnation with 20-80% (based on dry weight) of a 75-85% solids solution containing polyols, molecular weight 800-3500, aromatic polyisocyanates (NCO-OH 1.1-2:1), aromatic polyamines such as alpha,alpha prime-bi-p-toluidine or dichlorobenzidine with amine equivalent to 80-100% unreacted NCO, and 0.5-5% (based on polyol) catalyst.

8. Ansart, M.; Manguin, H. Cationic starches and polyelectrolytes; their role in paper manufacture. ATIP Rev. 24(2):61-6(1970); Fr.; ABIPC 41:A3024, A9226.

The introduction of ionic groups into starch which is added to screened stock, prior to entry to the headbox, improves the retention of fillers and of fines, and the mechanical properties and opacity of the paper produced. It also functions dramatically in reducing the amount of suspended matter in the white water. Various polyelectrolytes are discussed, including CMC, carboxymethyl starch, polyacrylamides, and dialdehyde starches.

9. Avis, R. P.; Scott Paper Co. Water-soluble, cationic, thermosetting resins for making cellulose sheet materials. Ger. Offen. pat. 2,050,529(March 9, 1972); CA 77:A20686.

The title resins were prepared by treating a polyalkylene polyamine with a urea to form a polyureide intermediate, treating the intermediate with a OH-containing compound and furthur treating with formaldehyde. Thus, urea was treated with triethylenetetramine and diethylenetriamine for 96 min at 148-50 C. The polyureide intermediate was cooled to 127 C and treated with formaldehyde; the mixture was cooled to 75 C and treated with phosphoric acid to form a viscous sirup. The sirup was further treated with HCHO, NaOH, and water. The resultant polyureide-formaldehyde resin had viscosity 49.5 cSt (25 C), pH 6.3, and 29.5% solids content. When 2% of the resin was incorporated into a manufactured paper sheet, the wet strength was 439 g/cm and dry strength 1910 g/cm compared with 40.2 and 1520, respectively, for a control without the resin.

10. Bankert, R. A.; Hercules Inc. Diallylamine-amide-polyaldehyde resins having utility as wet and dry strengthening agents in papermaking. U.S. pat. 3,728,216(April 17, 1973); ABIPC 44:A4586.

The wet and dry strengths of paper are improved by including in the stock a resin prepared from diallylamine, an amide such as bromoacetamide, and a polyaldehyde such as glyoxal.

11. Baranova, V. N.; Plisko, E. A.; Nud'ga, L. A.; Institute of High-Molecular Weight Compounds, Academy of Sciences, U.S.S.R.; All-Union Scientific Industrial Enterprises of the Cellulose-Paper Industry. Strengthening of paper containing cellulose. USSR pat. 424,933(April 25, 1974); Otkryt., Izobret., Prom. Obraztsy, Tovarnye Znaki 51(15):99(1974); CA 81:A171815.

For increasing the physicomechanical indexes of paper, the paper web is surface-impregnated with 1-2% solution of chitosan in AcOH with subsequent drying.

12. Berg, R. G.; Tate, B. E.; Pfizer, Chas., & Co. Inc. Use of polyamides derived from iminodiacetic acid and related compounds in improving the wet and dry strength of paper. U.S. pat. 3,526,608(Sept. 1, 1970); ABIPC 41:A10927.

The wet and dry strengths of paper are improved by incorporating into the paper or papermaking stock a product obtained by condensing epichlorohydrin with a polyamide prepared by reacting iminodiacetic acid or related compound with a polyalkylenepolyamine.

13. Blank, M. G. Effect of polymeric additives on the strength of papers with various compositions. Nauch. Tr. Leningrad. Lesotekh. Akad. (158):53-60 (1973); Russ.; Ref. Zh., Khim. (4):abstr. S1301(1974); CA 81:A171737.

Title only translated.

14. Blank, M. G.; Nyuksha, Yu. P. Effects of some vinyl polymers on paper strength. Prichiny Razrusheniya Pamyatnikov Pis'mennosti Pechati, Akad. Nauk SSSR, Lab. Konserv. Restavratsii Dok. 1967:123-34; Russ.; CA 67:A91839.

Paper stock containing 75% groundwood and 25% sulfite pulp gives, combined with vinyl polymers, paper of increased strength. The maximum strength increase is obtained by combined use of a copolymer dispersion of vinyl acetate with dibutyl maleate (I) and polyacrylamide. Parallel tests with both dispersions give better results for (I) before and after thermal aging. High strength improvement (10-15X) is obtained by introducing (I) in an amount of 50 weight percent of the dry fibers. Papers containing such a high percentage of additives lose 20-50% of their strength after thermal aging. Parallel tests with papers from cotton pulp prove, unlike papers containing groundwood, that (I) and polyvinyl acetate dispersions give the same results. The maximum folding endurance of cotton papers is obtained by combined use of a (I)-polyvinyl acetate dispersion (50% by weight of dry fibers) and polyacrylamide. Because of high strength loss after aging, it is best, for maximum strength and durability, to add a 4% polyvinyl acetate dispersion or (I) and 1% polyacrylamide to the cotton pulp. Addition of a high-viscosity polyacrylamide, applied after alum, is recommended.

15. Breen, D. L.; Frisque, A. J.; Nalco Chemical Co. Method of making improved paper and paper products. U.S. pat. 3,902,958(Sept. 2, 1975); ABIPC 46:A7718.

Paper of improved properties is obtained by adding to the papermaking stock a dispersion of a water-soluble anionic vinyl addition polymer and a water-soluble cationic polymer. The anionic polymer can be formed from acrylamide and acrylic acid; the cationic polymer can be formed from acrylamide and dimethylamino ethyl methacrylate. Different effects (e.g., wet and dry strength) can be achieved, depending on the nature and amount of the polymers added.

16. Buttrick, G. W.; Welch, F. J.; Eldred, N. R.; Union Carbide Corp. Paper products. Can. pat. 773,460(Dec. 12, 1967); ABIPC 38:A9652.

The physical properties (e.g., dry and wet strength) of paper are improved by incorporating in the paper an adduct of polyacrolein and a bisulfite such as sodium bisulfite.

17. Carr, M. E.; Hofreiter, B. T.; Hamerstrand, G. E.; Russell, C. R. Interpolymer from starch xanthate and polyamide-polyamine-epichlorohydrin resin in linerboard and newsprint. Tappi 57(10):127-9(1974); Engl.; CA 83:A62202.

In situ formation of an interpolymer from 0.25% Kymene 557 (polyamide-polyamine-epichlorohydrin resin) and 2.5% starch xanthate in an unbleached kraft handsheet furnished increased wet strength ninefold and dry strength 50% over untreated control paper. Repulpability of treated papers was not different from that of untreated papers.

18. Chan, L.-L.; Amy, J. E.; Borden, Inc. Polyalkylene amine-polyamide resins. So. African pat. 72 03,927(March 22, 1973); CA 80:A84918.

A long-chain water-soluble polyamide, suitable for treatment with an epoxy compound to give a wet-strength paper resin, was prepared by the reaction at 80-95 C of a C(sub 4-8) polyalkylene polyamine with a dimethyl C(sub 4-6) dialkanoate. Thus, a mixture of 108.0 g diethylenetriamine and 160 g dimethyl glutarate was refluxed at 90 C for 3 hr, and the temperature was gradually increased to 105 C and held for 3 hr to strip off the MeOH. When the Brookfield viscosity reached 100,000 cp at 105 C, 200 ml water was added to give a diethylenetriamine-dimethyl glutarate polymer (I) solution with solids content 53.6% pH 10.2, and viscosity at 25 C 340 cp (Brookfield LV2, 60 rpm). A mixture of 155.0 g polyamide solution, 150.0 ml water, and 40.6 g epichlorohydrin was heated at 50-5 C to viscosity 155 cp, diluted with 300 ml water, and the pH adjusted to 5.0 with HCl to give a solution of cationic epoxypropylated (I) with solids 15.8% and Brookfield viscosity 45 cp at 25 C. Addition of 1.25% aqueous epoxypropylated (I) solution to a 1:1 bleached sulfite-kraft pulp at 0.25% consistency and pH 7.0, followed by sheet formation and drying at 220 F gave sheets with good color and good wet and dry tensile strengths.

19. Chem 26 - Paper Processing. [Paper] industry finds new use for resin. ''Chem 26'' 5(1):28-31(Jan., 1969); ABIPC 39:A9693.

The paper industry has found a new application for Kymene 557 resin (Hercules Inc.), largely used as a wet-strengthening agent. The resin is a key ingredient in a dry strength retention system. High dry strength is achieved in paper and paperboard by adding separately unmodified cooked potato starch to thick stock (2% consistency), alum (aluminum sulfate), and Kymene 557 resin. Separate addition of starch and Kymene increased substantially the retention of fillers.

20. Chemirad Corp. Fibrous cellulose products treated with aminoplasts and polymers. Brit. pat. 1,125,792(Aug. 28, 1968); ABIPC 39:A7836.

A process for making paper of improved properties (particularly increased strength and stiffness) comprises adding to the papermaking stock a water-soluble aminoplast resin (e.g., a MF resin) and a polyalkylenimine such as PEI at a pH of at least 6.55.

21. Chite, R.; Fukuoka Paper Mfg. Co., Ltd. Water-resistant paper. Jap. pat. 71 42,041(Dec. 13, 1971); CA 77:A103584.

An asphalt emulsion containing a cross-linkable protective colloid, e.g., modified starch, cellulose, or polyvinyl alcohol, was added to a pulp dispersion, and the mixture was made into paper with good dry and wet strength. Thus, a mixture of starch 10, 2-4% NaOH 200, and N-methylolacrylamide 5 parts was heated 120 min at 70 C to give N-methylolcarbamylethyl starch (I). A mixture of water 100, asphalt 20, an emulsifier 0.3, and (I) 0.8 part or more was emulsified at 70 C to give a stable emulsion. The emulsion was added to a bleached kraft pulp dispersion with alum earth, and the dispersion was made into paper, which was sprayed with an ammonium chloride solution and dried 10 min at 110 C. The paper had dry strength 5.2 times that of similar paper without the emulsion and wet strength 8.7 times that of similar paper with an emulsion without (I); compared with 3.6 and 3.4 times, respectively, for paper with emulsion stabilized with untreated starch.

22. Cloke, I. J.; Bailey, B. E.; International Synthetic Rubber Co. Ltd. Elastomer-containing nonwoven paper or fabrics. Brit. pat. 1,239,902(July 21, 1971); CA 75:A153140.

The drape, handle, and tensile, burst, and tear strengths of nonwoven fabrics or papers prepared from slurries of cellulose, nylon, and (or) rayon fibers are improved if the slurries are treated with a 16:1:3 butadiene-hydroxypropyl methacrylate-styrene copolymer (I) latex, a 16:1:3 butadiene-tert-butyl hydroxypropyl maleate-styrene copolymer latex, a 14:1:5 butadiene-N-methylolacrylamide-styrene copolymer latex, or a similar latex. Thus, a slurry of cellulose fibers is treated with a 16:1:3 (I) latex to deposit 20% dry (I) on the fibers and then made into paper with good drape and a soft handle, having tensile strength 10 lb/inch, burst strength 30 lb/inch, and tear strength 150 g, compared with 8 lb/inch, 10 lb/inch, and 80 g, respectively, for paper containing no (I).

23. Coscia, A. T.; Williams, L. L.; American Cyanamid Co. Water-soluble, ionic, glyoxylated, vinylamide, wet-strength resin and paper made therewith. U.S. pat. 3,556,932(Jan. 19, 1971); ABIPC 42:A991.

The wet and dry strength properties of paper are improved by treating the paper with a glyoxal-reacted vinylamide polymer, such as acrylamide-diallyldimethyl ammonium chloride. The treated paper can be easily repulped under slightly alkaline conditions.

24. CPPA Technical Section. Dry and wet tensile breaking strength and stretch of creped papers. CPPA Std. D.32P, June, 1974. 2 p.; ABIPC 46:A4689.

This method is for the determination of the dry and water-saturated tensile breaking strengths and machine-direction stretch of creped papers containing 10% or more stretch. The dry tensile breaking strength is the maximum weight or load that the specimen will support before pulling apart. The wet tensile breaking strength is the tensile strength of the specimen immediately after complete saturation with water. Machine-direction stretch is the percent elongation of the specimen strip at the peak dry tensile load during testing to failure. These properties define the essential functional strengths and conformability characteristics of such creped papers as facial and toilet tissues, serviettes (napkins), and towels.

25. Cruz, M. M.; FMC Corp. Starch monothiocarbonate disulfide and process for using same in paper. U.S. pat. 3,411,984(Nov. 19, 1968); ABIPC 39:A8823.

The wet and dry strength of paper is improved by adding to the stock a starch monothiocarbonate disulfide produced by oxidizing starch dithiocarbonate disulfide (starch xanthide) with chlorine dioxide.

26. Dahl, R.; Anchor Continental Inc. Polyurethane composition for impregnating paper. Ger. Offen. pat. 2,209,529(Sept. 20, 1973); CA 80:A27869.

The dry and wet strength of porous substrates, particularly paper, is increased by impregnation with a 20-30% solution of isocyanate-terminated polyol containing a tin compound catalyst to uptake 20-80%, drying, and curing. Thus, a mixture of polyether triol (Niax Triol LHT 112, molecular weight 1500) 104, Niax Triol LHT 67 (molecular weight 2500) 26.3, toluene diisocyanate 38.5, C(sub 7)H(sub 16) 51.2, and toluene 120 kg is heated 1 hr at 82-93 C and 16 hr at 27 C, combined with 1.36 kg stannous octanoate, impregnated in paper to uptake approximately 50%, and dried and cured 1.5-3 min at 52-177 C to give a product having good flexibility and improved dry and wet strength.

27. Dahl, R.; Anchor Continental Inc. Polyurethane polymer impregnation of paper. Brit. pat. 1,388,416(March 26, 1975); CA 83:A117490.

A urethane composition for impregnating paper backing for adhesive tapes giving a uniformly flexible product with good wet and dry strength and delamination resistance was manufactured by treating 20 lb Niax Triol LHT 112 3 hr at 100 C with 3.5 lb tolylenediisocyanate, adding 30 lb toluene, 1.5 lb of the bis(phenol) adduct of methylene bis(4-phenylisocyanate), 540 g stannous octoate, and 54 g triethylamine. The mix was coated onto paper, and cured approximately 30 sec at 300-20 F to evaporate solvent and give the bis(phenol)-methylene bis(4-phenylisocyanate)-Niax Triol LHT 112-tolylenediisocyanate copolymer.

28. Dyck, A. W. J. Chemical additives – the papermakers' future. Am. Paper Ind. 52(10):19, 22-3(Oct., 1970); ABIPC 41:A9232.

Developments in papermaking chemical additives are reviewed, including filler pigments, wet- and dry-strength additives, softeners, alkaline or neutral sizes, and liquid dyes. Future developments in papermaking chemicals are also outlined.

29. Dyck, A. W. J. Focus on stock preparation. Am. Paper Ind. 53(6):33-4, 36(June, 1971); ABIPC 42:A3834.

Stock treatment in pulpers, deflakers, beaters, conical refiners, and disk refiners is briefly reviewed and new developments and new fiber treatment concepts are pointed out. The role of and trends in additive use, including internal sizes, fillers (such as clays, titanium dioxide), dry- and wet-strength additives, and drainage and retention aids, are mentioned.

30. Dyck, A. W. J. Papermaking chemicals. Am. Paper Ind. 55(4):30-2; (8):42-4 (April, Aug., 1973); ABIPC 44:A6983.

Significant trends in the use and consumption of papermaking chemicals are discussed. Usage of salt cake and sodium carbonate is declining, while use of

NaOH is on the rise in the pulping area. Rapid growth in use of chlorine dioxide continues. Application of retention and drainage aids is increasing. Clays continue to dominate the filler and coating pigment markets, with much R&D work being directed at meeting more rigid specifications for printing paper properties. There has been an increase in use of synthetic sizes at the expense of rosin sizes. Starches continue to dominate as pigment binders, while synthetic binder use increases and use of proteins declines. Other materials discussed are wet- and dry-strength additives, polymeric pigments, reprographic coating materials, and dyes.

31. Economou, P.; American Cyanamid Co. Amphoteric strengthening agents for paper. U.S. pat. 3,660,338(May 2, 1972); ABIPC 43:A6879.

This invention provides a composition consisting of an ionically self-cross-linked polysalt and a water-soluble ionization suppressor. The polysalt can be formed from an acrylamide/acrylic acid copolymer, and a methylamine/ammonia/epichlorohydrin condensate; the suppressor can be magnesium sulfate. The suppressor prevents coacervation of the polysalt until the composition is diluted to about 0.1-0.001% solids. The composition is suitable for addition to papermaking stock as a strengthening agent.

32. Economou, P.; American Cyanamid Co. Amphoteric strengthening agents for paper. U.S. pat. 3,790,514(Feb. 5, 1974); CA 81:A39302.

A water-soluble ionization suppressor, ionization constant greater than 10(exp -6), was added to an ionically self-cross-linked polysalt solution, formed by mixing a water-soluble polyanionic polymer and a water-soluble cationic polymer 1 of which had an ionization constant less than 10(exp -3), in sufficient amount to prevent coacervation of the polysalt at 1-10% concentration but insufficient to prevent coacervation at 0.1-0.001% concentration. Addition of the polysalt solution to a papermaking pulp at pH 6-8 caused the formation of a haze of colloidal droplets of polysalt coacervate which were adsorbed onto the cellulose fibers and gave paper with increased strength. The ionization suppressors sodium sulfate, sodium chloride, sodium hydrogenphosphate, or sulfuric acid were added to an aqueous solution of either acrylamide-acrylic acid copolymer (I) or adipic acid-epichlorohydrin-tetraethylenepentamine copolymer (II). The weight ratio in the final mixed solution was 55:45 (I)-(II) and the suppressor was present at 5-45% polymer weight. The polysalt composition was stable 10 or more days at 20 C at 25% solids and was diluted to 2% concentration without haze formation. A haze developed on dilution to less than 0.1% solids. Dry paper strength was increased 20-60% by addition of sufficient polysalt solution to a cellulose suspension at pH 6 to give 0.5% polysalt based on dry fiber weight.

33. Economou, P.; American Cyanamid Co. Manufacture of improved dry strength paper. Brit. pat. 1,184,807(March 18, 1970); ABIPC 41:A3767.

Paper of improved dry strength is formed by heating (at 190-250 F) and drying the sheet formed from an aqueous suspension containing the papermaking fibers and an aqueous solution of a composition including an ionically self-cross-linked coacervating liquid ampholytic polysalt of a water-soluble polyanionic polymer with a water-soluble polycationic polymer, the composition including a water-soluble ionization suppressor to render the polysalt water-soluble. The polysalt, for example, can be formed from an acrylamide:acrylic acid copolymer and polyacrylamide-ethylenediamine, with sodium sulfate as the ionization suppressor.

34. Economou, P.; American Cyanamid Co. Reinforcement agents for paper. Fr. pat. 1,521,163(April 12, 1968); CA 71:A40511.

Water-soluble amphoteric polysalts are prepared from a water-soluble anionic polymer, a water-soluble cationic polymer, and a salt such as sodium sulfate, sodium chloride, sodium acid phosphate, magnesium sulfate, calcium chloride, or potassium trichloroacetate and added (0.5% based on dry fibers) to cellulose pulp used for the preparation of paper. The polysalts have a coacervation effect and give paper having 20-60% greater dry burst strength compared with untreated paper. Treatment of the pulp with a small amount of aluminum sulfate before the addition of the polysalt gives a further slight improvement in the dry burst strength of the paper. The anionic polymer is a 9:1 acrylamide-acrylic acid copolymer (I), an 8:3:9 acrylamide-maleic anhydride-styrene copolymer, or a similar polymer. The cationic polymer is a 1:1 adipic acid-tetraethylenepentamine copolymer (II) condensed with 15 mole percent epichlorohydrin, a reaction product of 7 parts polyacrylamide and 42 parts ethylenediamine, a 9:1 acrylamide-dimethylpyridine copolymer quaternized with methyl sulfate, or a similar polymer. Thus, a 10-40% aqueous solution of 11 parts (I) and 9 parts (II) (condensed with 15 mole percent epichlorohydrin) containing 6.7 parts sodium sulfate was added (0.5% polysalt based on dry fibers) to cellulose pulp at pH 6. The pulp was made into paper and dried at 88-121 C. The burst strength of the paper was 20-60% greater than that of control paper containing no polysalt.

35. Economou, P.; Hardy, J. F.; Renner, A.; Forster, E.; Diethelm, H.; Cabot Corp.; Ciba-Geigy AG. Paper containing a filler based on urea-formaldehyde resin. Ger. Offen pat. 2,100,907(Oct. 14, 1971); CA 76:A2611.

Paper containing 10-25% of a 1:1-2 formaldehyde-urea resin (I) with a surface area 5-100 sq m/g had improved strength. Paper, prepared from sulfide cellulose of mill grade (CF) 381 ml containing 10% (I) (2 sq m/g surface area and containing 10.8% volatiles) and pigments exhibited an 18.6 dry strength [corrected to 22.8 kg basis weight, TAPPI T 404 os-61], 87.8% whiteness (TAPPI T 452 m-58), and 74.4% opacity (corrected to 22.8 kg basis weight).

36. Eldred, N. R. Paper additives and resins. Encycl. Polym. Sci. Technol. 9:748-93(1968); Engl.; CA 70:A79267.

A discussion is given of the use of polymers in paper manufacture and conversion, covering wet-strength resins, formation and retention of dry strength, latexes for wet-end addition, sizing materials, additives for pigment coating, functional coatings, and corrugating materials. The techniques of paper saturation and formation of paper laminates are described as is the use of noncellulosic fibers. 70 references.

37. Espy, H. H.; Hercules Inc. Aminopolyamide-acrylamide-polyaldehyde resins employing an alpha,beta-unsaturated monobasic carboxylic acid or ester to make the aminopolyamide and their utility as wet and dry strengthening agents in papermaking. U.S. pat. 3,728,215(April 17, 1973); ABIPC 44:A4594.

The wet and dry strengths of paper are improved by including in the stock a resin prepared from a polyaldehyde such as glyoxal, acrylamide, and an aminopolyamide prepared by condensation of an alpha,beta-unsaturated monobasic carboxylic acid or ester such as methyl acrylate, and a polyalkylene polyamine such as polyethylene polyamine.

38. Espy, H. H.; Hercules Inc. Aminopolyamide-acrylamide-polyaldehyde resins having utility as wet and dry strength agents, retention aids and flocculants and a process of making and using them and paper made therefrom. U.S. pat. 3,607,622 (Sept. 21, 1971); ABIPC 42:A9389.

The title resin is prepared by reacting an unsaturated amide such as acrylamide with an aminopolyamide prepared by condensing a polyalkylenepolyamine such as tetraethylenepentamine with an organic polybasic carboxylic acid or anhydride such as adipic acid, and then reacting the resulting adduct with an aldehyde, such as glyoxal.

39. Espy, H. H.; Hercules Inc. Polyamine-acrylamide-polyaldehyde resins having utility as wet and dry strengthening agents in papermaking. U.S. pat. 3,728,214(April 17, 1973); ABIPC 44:A4595.

The wet and dry strengths of paper are improved by including in the stock a resin formed from a polyamine such as tetraethylenepentamine, acrylamide, and a polyaldehyde such as glyoxal.

40. Faessinger, R. W.; Scott Paper Co. Neutral cure wet strength resins prepared by polymerizing glyoxalolated acrylamide with further acrylamide and a basic, nitrogen-containing monomer. U.S. pat. 3,709,857(Jan. 9, 1973); ABIPC 44:A4596.

Resins of use as pulp additives to improve the wet and dry strength of paper are formed by reacting glyoxal with acrylamide and then polymerizing the product with acrylamide in the presence of a basic nitrogen-containing monomer such as N,N-dimethylaminoethylmethacrylate.

41. Fahmy, Y.; El-Saied, H. Chemical modification of pulp and physically added chemicals in papermaking. (2). Grafting copolymerization with hydrophilic and hydrophobic monomers and their binary mixtures in comparison to physically added homopolymers and to classical chemical modification. Holzforschung 28(2):61-6(April, 1974); Engl.; ABIPC 45:A4778.

At the same degree of hydroxyl substitution, graft polymerization of pulp with hydrophilic monomer (methacrylic acid) was less effective in improving paper dry strength than classical hydrophilic treatment of chemical pulp via carboxymethylation. Physical addition of sodium acrylate homopolymer to the pulp slurry prior to sheet formation was also less effective in improving strength than addition of sodium CMC. Pulp hydrophobization via graft polymerization with acrylonitrile increased opacity and water resistance, but reduced paper dry strength to a greater extent than classical chemical hydrophobization (acetylation). However, physical addition of acrylonitrile homopolymer to the pulp slurry before sheet formation followed by hot pressing brought about an increase in opacity and water resistance without reducing paper dry strength. It is concluded that physical addition of cellulose derivatives or synthetic resins to the pulp slurry prior to sheet formation is more effective than pulp modification by classical chemical means and by grafting. Classical chemical modification - as far as pulp types and methods used in this study are concerned - is more successful than graft polymerization. An exception is grafting with binary hydrophilic/hydrophobic monomer mixtures.

42. Farbenfabriken Bayer AG. Increasing the moisture resistance of paper. Fr. pat. 1,511,878(Feb. 2, 1968); CA 70:A69416.

Adipic acid-diethylenetriamine copolymers, adipic acid-triethylenetetramine copolymers (I), polyethylenimine, bis(3-aminopropyl)methylamine-epichlorohydrin copolymers, epichlorohydrin-ethylenediamine copolymers, and similar polyamides and polyimides having a high molecular weight are treated with MeOCH(sub 2)NCO (II), BuOCH(sub 2)NCO, or MeOCH(sub 2)NCS, and the reaction products are added to sulfite pulps. Paper prepared from these pulps has higher moisture resistance and greater wet and dry tensile strength, compared with untreated paper and paper containing a prior-art, commercial additive such as HCHO-urea resin or the reaction product of epichlorohydrin and (I). Thus, a mixture of adipic acid 292, diethylenetriamine 194, ethylenediamine 21.6, and water 100 g was heated under nitrogen at 180 C while distilling the water, heated at 185 C for 3 hr and at 180 C and 20-50 mm for 1 hr, cooled, and mixed with its own weight of water to give 850 g 50% aqueous polyamide solution. This solution (760 g) was diluted with 400 g water, treated slowly with 40 g butane 1,4-diglycidyl ether at 15 C, heated at 55 C to 150 cp viscosity, diluted with 900 g water, and stirred for 3 hr at 55 C. This solution (525 g) was treated slowly with 22 g (II) at 15-20 C, stirred for 1 hr, and mixed with 718 g water and 5 g AcOH. The solution had pH 7 and viscosity 13 cp. A 0.25% suspension (1 kg) of bleached sulfite pulp was treated with 0.1 g of the polymer solution prepared above, diluted with 6 kg water, and made into paper, which was heated at 110 C for 5 min. The paper had 15-40% greater wet and dry tensile strength and 4.5% greater moisture resistance than paper treated with a commercial reaction product of epichlorohydrin and (I).

43. Frolov, M. V.; Dobysh, Sz. V. Effect of chemical bonds between fibers on the wet strength of paper sheets. Papiripar 18(6):292-5(1974); Hung.; CA 83:A81647.

The wet strength of paper could be increased by replacing the hydrogen bonds [bond energy (E) = 4-4.5 kcal/mole] with ionic (E = 10-13 kcal/mole) or covalent bonds (E = 70-84 kcal/mole). A blend of aminoethyl cellulose (nitrogen content 8.2%) and 6-carboxy cellulose (carboxyl content 2.5%) in 1:1 ratio increased the dry and wet strength of paper by 20% and 14%, respectively. Blending the epoxidized cellulose (I) with unmodified (I) also increased the wet strength. The increasing degree of beating increased the active pulp surface affecting the bond formation between the fibers and consequently the wet strength of paper.

44. Fujita, T.; Kamaishi, T.; Urata, Y.; Toray Industries, Inc. Synthetic fiber pulp. Jap. Kokai pat. 74 117,721(Nov. 11, 1974); CA 82:A141885.

Maleated propylene polymers were emulsified in a noncompatible good and poor solvent mixture and flash-spun at a temperature higher than the solvent boiling point to give pulp substitute. For example, 30 g maleated polypropylene (1.2 molecules maleic anhydride/100 propylene units), 265 cc water, 225 cc dichloroethylene, 1.5 g sodium dodecyl sulfate, and 1.5 g calcium dodecyl sulfate were stirred in an autoclave and flash-spun at 140 C via a 1.6 mm-diameter nozzle, and the extrudate (40 g) was beaten with 0.03 g cationic starch and 750 cc water, mixed in 0.6:2.4 dry weight ratio with softwood-hardwood bleached kraft pulp mixture, and formed to a wet sheet which was then hot-calendered to give paper with higher breaking length and surface strength than that using isotactic polypropylene fiber in place of the maleated fiber. Maleated ethylene-propylene polymer fiber was also used.

45. Fujiya, J.; Ohtake, M.; Kato, S.; Denki Kagaku Kogyo KK. Paper strengthening agents. Jap. Kokai pat. 74 126,908(Dec. 5, 1974); CA 83:A12633.

Paper strengthening agents contained polyvinyl alcohol modified to carboxylic acid and amide content 0.5 mole% or more each (total modifier content 1-40 mole%). For example, a 0.5% bleached hardwood kraft pulp slurry was mixed with filler 20, rosin size 1, and saponified acrylamide-vinyl acetate polymer (I) (amide content 4.5 mole%, carboxylic acid content 3.5 mole%) 1% (based on pulp weight), treated with alum to pH 4.5, and formed to paper with breaking length 3 km, burst factor 2.17, and folding endurance 134 cycles, compared with 2.03, 1.33, and 55, respectively, for paper not containing saponified (I).

46. Gaertner, V. R.; Monsanto Co. Polyglycidylpolyamine-treated polysaccharides. U.S. pat. 3,361,590(Jan. 2, 1968); ABIPC 39:A3160.

Cellulosic materials, including paper, are improved in wet and dry strength and dimensional stability by treatment with polyalkylene amines, such as N-(n-octadecyl), N,N',N'-tris(2,3-epoxypropyl), 1,3-propylenediamine.

47. Gaertner, V. R.; Monsanto Co. Water-soluble nitrogen prepolymer compositions for treating paper and textiles and modifying starch. U.S. pat. 3,314,897(April 18, 1967); CA 67:A23075.

Water-soluble organic nitrogen prepolymer compositions which are cross-linkable when cured and improve the physical and chemical characteristics of polysaccharides are especially useful for sizing paper and improving its wet and dry tensile strength and dimensional stability, for waterproofing cellulosic textiles and improving their crease resistance, and as starch-modifying agents. The prepolymer comprises 2-4 components, one of which is a simple prepolymer of an aliphatic amine-epihalohydrin adduct and an aliphatic amine, the other components being amines, adducts, or other prepolymers. Thus, 7.05 g of a tallow N-alkenyl- and N-alkyl-1,3-propanediamine (I, Duomeen T) was added to 25 g of a cold MeOH solution containing 8.4 g of an adduct (neutralization equivalent 342) of (I) with 3 moles epichlorohydrin (II) and the mixture refluxed at 67 C for 1 hr to give a simple prepolymer solution (III). To (III), 13.9 g of a cold MeOH solution containing 7.2 g of an adduct (neutralization equivalent 199) of diethylenetriamine (IV) with 5 moles (II) was added and the mixture was refluxed at 67 C for 2.5 hr to give a prepolymer solution (IV) having 74% of its original basic nitrogen titer unneutralized. (IV) (1 wt.%) was applied to a refined bleached Gatineau pulp slurry, the treated pulp sheeted into paper, dried, and aged for 14 days at ambient conditions to give a paper having excellent sizing (3000 sec by the ink-flotation method) and dry tensile strength 68% of an untreated sheet compared with paper sheets treated with (III) alone, which gave a very hard sizing of greater than 6000 sec, but only 53% of dry tensile strength. A decrease in titer was obtained by using (I) hydrogenated over finely divided palladium and rhodium on charcoal and aluminum oxide.

48. Goncharova, V. P.; Gulyaeva, R. M. Paper pulp. USSR pat 294,899(Feb. 4, 1971); Otkryt., Izobret., Prom. Obraztsy, Tovarnye Znaki 48(7):88(1971); CA 75:A99343.

A rigid polymer dispersion is added to beaten, sized, and filled pulp to increase the tensile strength of the paper without reducing the whiteness. Polyacrylonitrile or polyurethane is used at 5-15% of the dry fiber weight.

49. Griggs, W. H.; Eastman Kodak Co. Photographic paper and method for its manufacture. Can. pat. 871,604(May 25, 1971); ABIPC 42:A10783.

Paper of good wet and dry strength, of use as a photographic base, is formed from stock to which has been added 0.001-0.006 part per part fibers on dry weight basis of a cationic thermosetting amino-aldehyde wet-strength resin, 0.003-0.01 part of a cationic thermosetting polyamide-epichlorohydrin wet-strength resin, and 0.004-0.015 part of an anionic polyacrylamide dry-strength resin. The first resin can be MF, the second can be formed from diethylenetriamine, adipic acid, and epichlorohydrin, and the third can be a copolymer of acrylamide and acrylic acid.

50. Griggs, W. H.; Eastman Kodak Co. Photographic paper comprising a cationic amino aldehyde resin and a cationic polyamide-epichlorohydrin resin and an anionic polyacrylamide dry strength resin and method for its manufacture. U.S. pat. 3,592,731(July 13, 1971); ABIPC 42:A8534.

A photographic paper base includes a cationic thermosetting amino-aldehyde wet-strength resin, a cationic thermosetting polyamide-epichlorohydrin wet-strength resin, and an anionic polyacrylamide dry-strength resin. The resins are added before sheet formation. This combination of resins gives adequate strength properties while providing an aldehyde concentration which is great enough to provide the desired hardening of photographic emulsion applied to the paper base without affecting its sensitivity.

51. Griggs, W. H.; Eastman Kodak Co. Wet and dry strength and liquid repellency of fibrous material. Can. pat. 873,777(June 22, 1971); ABIPC 42:A11886.

The wet and dry strength of paper and its resistance to penetration by liquids are increased by treating the paper with an amine oxide swelling agent such as N-methylmorpholine-N-oxide, applying an alkylketene dimer sizing agent, heating to swell the fibers, and removing the amine oxide by evaporation, washing, or solvent extraction.

52. Griggs, W. H.; Eastman Kodak Co. Wet and dry strength and liquid repellency of fibrous material. U.S. pat. 3,503,700(March 31, 1970); ABIPC 41:A1789.

The wet and dry strength of paper is increased by treatment with amine oxides such as N-methylmorpholine-N-oxide, and simultaneously the water repellency is increased by treatment with alkylketene dimers. The different agents do not interfere with the effectiveness of each other.

53. Gunder, W.; Lenz, J.; Brunnmuller, F.; Badische Anilin- & Soda-Fabrik AG. Wet- and dry-strength agent for paper. Ger. pat. 2,301,035(DOS July 18, 1974); ABIPC 46:A899.

Sulfite- and/or bisulfite-modified MF condensation products are claimed as wet- and dry-strength agents for paper. The particular products described are especially designed to permit surface treatment of formed paper webs, rather than beater addition.