The Institute of Paper Chemistry

Appleton, Wisconsin

Doctor's Dissertation

The System of Rosin Size, Alum, and Fiber as Related to Problems in Paper Sizing

by Samuel J. Robinson

June, 1934
THE SYSTEM OF ROSIN SIZED, AWM, AND FIBER AS RELATED TO PROBLEMS IN PAPER SIZING

A thesis submitted by

Samuel J. Robinson

B.S., 1931, Iowa State College
M.S., 1932, Institute of Paper Chemistry

in partial fulfillment of the requirements
of the Institute of Paper Chemistry for
the degree of Doctor of Philosophy from
Lawrence College, Appleton, Wisconsin

June, 1936

PROPERTY

INSTITUTE OF PAPER CHEMISTRY
Appleton, Wisconsin
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CHAPTER I.

INTRODUCTION

The sizing of paper represents one of the important steps in the manufacture of various grades of paper. The chief process of sizing paper consists in the addition of resin size and alum to the beater containing fiber stock. Under these conditions the resin size and alum may undergo various reactions and enter into numerous chemical and physical equilibria, not the least of which involves a certain amount of hydrolysis; the colloidal nature of the resin and cellulose fibers may alter any classical chemical reactions and the impurities accompanying the resin, alum, pulp, and water may greatly influence the sizing mechanism. Moreover, at every step in the manufacture of paper from the time that the resin size is added to the beater until the paper has passed through the calendar stacks variables may enter to greatly influence the size characteristics of the finished sheet. Some of the products which investigators have suggested as the true sizing agents are free resin; aluminum resinate, basic or acid alumina resinate, basic aluminum sulfate and alumina, either singly or in various combinations with each other.

In view of the variable source and nature of the materials and variables in the manufacturing process, the problem of resin sizing must be investigated stepwise, simplifying the system as much as possible.
beginning at the fundamentals, using chemically pure materials and
keeping all conditions under definite control.

The first step in this method of attack was made by
Bialkowski (5) when he investigated the degree of hydrolysis of sodium
abiate solutions and the effect of cellulose fibers on dilute sodium
hydroxide and sodium abiate solutions. The next step in continu-
ing these studies is the addition of aluminum sulfate to the above
system. The particular phase of the problem covered by this investi-
gation includes the effect of excess aluminum sulfate solutions on
dilute sodium abiate solutions in the absence and presence of pulp
fibers and a comparison of the relative ease of sizing of various
pulps in relation to their behavior to sodium abiate and aluminum
sulfate solutions.
CHAPTER II.

HISTORICAL SURVEY

In 1807 Moritz Illich introduced his process for sizing paper in the beater; previous to that time all paper was sized by a surface treatment. However, it was not until 1820, when the paper machine was introduced and paper production increased, that Illich's process was extensively adopted. Today the greatest portion of our paper is made in the same way and the procedure is very little changed from that which Illich introduced. He advanced the theory that in order to resin size paper, the water insoluble resin must be converted into a water soluble substance; it must be thoroughly mixed with the fibers and then rendered insoluble so that the resin regains its original properties. Thus the first theory of resin sizing held free resin to be the active sizing agent. With the rapid advancements made in chemistry and with a better understanding of chemical reactions, the aluminum rosinate theory was widely adopted. Later, with a better understanding of colloidal chemistry, various colloidal theories of sizing were introduced to explain the mechanism of resin sizing. The literature now available on the subject is quite voluminous and frequently contradictory opinions on many essential points are given.
Aluminum Resinate Theory. Arledter (3) states as a result of his experimental work that aluminum resinate are precipitated from the size by alum and that these in turn are then decomposed by the heat of the drying rolls. The resinate acids melt and fill the pores of the paper, causing it to be sized.

Remington, Donack and Davidson (45) studied aluminum resinate prepared by treating a neutral resin soap with $\text{Al}_2(\text{SO}_4)_3$. The air dried neutral aluminum resinate contained 3.95 per cent $\text{Al}_2\text{O}_3$ while the theoretical $\text{Al}_2\text{O}_3$ is 4.96 percent. The dry compound is readily soluble in cold benzene and chloroform and partially soluble in ether and alcohol. The authors contradict the older theory that free resin acids are effective agents in sizing of paper and advance the hypothesis that aluminum resinate is the active sizing agent. They suggest that it is probably more or less chemically combined with the cellulose of the paper and that part of the aluminum resinate may be dissociated and extracted by ether or ethyl alcohol. This lends plausibility to the free resin acid theory. Free resin alone was not believed to be a suitable sizing agent.

Heuser (28) worked with sodium resinate and alum in the absence of fiber and concluded that no basic sulfates were formed. If equivalent quantities react a precipitate of neutral aluminum resinate is formed ($\text{Al}_2\text{O}_3$; calculated 5.9% - found 5.9%). There was no aluminum in the filtrate. Immediately after drying at 80°C, it is soluble in
in ether, chloroform and benzene, but not in alcohol. The aluminum resinate shows no definite melting point but turns brown and decomposes at 115° C. By extraction of the neutral resinate with absolute alcohol never more than 56.66% was dissolved and all of the $\text{Al}_2\text{O}_3$ remained in the residue which was insoluble in ether.

Ellingson (19) prepared numerous metallic salts of abietic acid and found that aluminum was one of the few metals that formed a neutral salt with abietic acid. He reports 5.54% percent $\text{Al}_2\text{O}_3$; the theoretical percentage being 5.50 percent. Belitzer (6) came to the conclusion that aluminum resinate is the most important sizing agent. Schutz and Klumitt (89) precipitated neutral sodium resinate and sodium abietate with excess alum and in all cases they found from analysis for $\text{Al}_2\text{O}_3$ that the neutral aluminium resinate or abietate was formed. From their work they conclude that free resin does not exist as such but is converted into the sodium acid salt, this salt reacting with alum to form the neutral aluminum abietate. They claim that the pulp fibers have no effect on the sizing reaction. Rozscher (85) states that the acidity during sizing determines whether sizing is due to free resin or aluminum resinate. He considers the bound resin to be more important in sizing than the free resin and aluminum ions.

De Gee (12) considers that free resin size is an acid resinate of an alkali and that an acid resinate of aluminum is the important sizing agent. This is formed from a neutral resinate only when a large excess of alum is added. The necessity for alum is not
so much to form the acid resinate as it is to precipitate the resin in a more colloidal state than would result from the use of other precipitants. Edge (15) found that two percent dry precipitated acid aluminum resinate added to a moderately "not" pulp at a pH of 5.0 in the presence of a little alum gave hard sized paper. The same effect was obtained with commercial aluminum resinate, but normal aluminum resinate, purified with ether, did not give hard sizing.

Aschan (6) states that the sizing deposit consists of a mixture of aluminum resinate, free resin acids and a little free aluminum hydroxide. The free resin acids can be extracted with ether. An excess of the free acid is not an effective substitute for aluminum resinate. Griffin (21) maintains that free resin, aluminum resinate and alumina are all necessary for good sizing and that neither free resin nor aluminum resinate alone are adequate. He found that paper which had been treated with HCl, washed and air dried was very absorbent before any resin had been extracted and from this evidence concluded that free resin was not an effective sizing agent. Paper made with alum but without size, and paper in which the size was precipitated by $\text{H}_2\text{SO}_4$ were unsized, but if aluminum hydroxide was added to the stock in which the size had been precipitated by $\text{H}_2\text{SO}_4$, the paper was better sized, even though the Al(OH)$_3$ was only stirred in by hand for a few minutes. From this work he concluded that cellulose hydrates do not seem to combine directly to the extent of being sized, with either free resin acids or alumina, and that alum precipitates the size as a resinate, paper being sized by the resinate, resin and alumina.
separately. Sieber (94) claims that it is quite possible that aluminum resinate as such, is formed and that it exerts a certain sizing action on the fibers of paper but that there is also a possibility that alumina absorbs free resin holding it in combination which resists dissolution. Osman (39) found that freshly prepared aluminum resinate dried without heat was completely soluble in ether, benzene, and carbon tetrachloride but insoluble in alcohol, which decomposed it, dissolving only a portion of the free resin acids. Heat also decomposed it, and the ether dissolves only part of the free acid leaving aluminum resinate undissolved. Acidity equal to a pH of 3.5 liberates considerable free acid. An ether solution of aluminum resinate also has sizing properties, but its results are inferior to those when part of the free resin is liberated with alum or sulphuric acid.

Robscher (67) expresses the opinion that aluminum resinate, aluminum hydroxide and free resin all play an important part in sizing, and that free resin and adsorbed aluminum ions alone cannot account for sizing. He found the degree of sizing to be independent of the pH of the stock, being due to adsorption of free resin and being impaired, rather than improved, by free aluminum hydroxide.

Hunghenower (37) states that sizing was due to both free resin and basic aluminum resinate. The greater the excess of alum the higher the percent of free resin and the more basic the aluminum resinate; but the maximum free resin was forty-one percent even when twelve times the theoretical amount of alum was used. He claims that free resin in paper may be extracted by alcohol of 0.674 sp. gr.
This does not dissolve basic aluminum resinate; but ether will dissolve both. Edge (17) states that the precipitates obtained by adding alum and sulphuric acid to colloidal resin solutions have ash contents and other solubilities of the same order as those of precipitates from sodium resinate solutions under similar conditions.

Zhereboff (67) disagrees with Warster's theory that all resin is precipitated as free resin in the presence of excess alum. He states that aluminum resinate is present in the beater, on the wire, and in the paper itself, and that the accompanying free resin amounts to only 10 - 50 percent of the total used. He (66) disagrees with the colloidal theory of Sieber, Lorsche, Stockigt and Klinger. Zhereboff states that although the sizing solution is colloidal, the active sizing acid of colophony are crystalloidal. If the union of alumina and resin is merely an adsorption of one colloid on another, then the amount of aluminum oxide in the combination should vary. But he refers to the results of Remington, Heuser, and Sieber showing nearly the same amount of aluminum oxide, namely 4.78 to 5.69 percent, making allowance for variation in the acid number of different resins. He concludes that only those resin compounds which possess chemical activity, that is, have double bonds, are useful in sizing. He points out that the fact that paper does not lose its sizing after many years suggests a chemical combination between cellulose and resin.

Free Resin Theory. Bray (11) considers that a high free resin size is the best to use, but offers no convincing evidence in
proof of his claim. From his work, he finds that more alum is necessary in the presence of cellulose. Maximum sizing is obtained with a resin - alum ratio of 1:12 when 3.5 to 4.0 percent alum was used.

Arnold (5) states that free resin is the ultimate sizing agent and suggests that the alum first reacts to form aluminum resinate which in turn is partially or totally transformed into free resin by the action of excess alum. Gaunyey (22) claims that under conditions existing in the mill no aluminum resinate is precipitated in the paper.

He bases his conclusions on the ash shown by the paper before and after extraction with ether, and from the results of extracting first with 65 percent alcohol and then with ether andashing the latter extract.

Haug (24) claims that when sodium resinate is highly diluted with distilled water it undergoes hydrolysis to an extent of approximately one hundred percent. His results are based on chemical tests and conductivity measurements. Ivanov (29) concludes that all resin is in a free condition at better concentrations and at a dilution of 0.5 grams of resin per liter, as much as 95 percent of the resin is free. Thiriet and Delcroix (61) claim that free resin is the active sizing agent and that resin is made into soap so as to obtain the required degree of subdivision. Free resin in size is of advantage only as it reduces the alkali consumption, and it does not give any better results than neutral size if the pH of the stock at the paper machine is 4.5 to 5.0.

Usme (64) rejects Klamm's theory of the action of heat in
drying paper and believes that the higher temperature favors the formation of a basic resinate and its complex with free acid. Since the extraction of sized paper with alcohol removes free resin and reduces sizing it seems to show that free resin has sizing power.

Wiegler (65) favors a free resin size and claims that resin particles one micron in diameter give optimum sizing.

Malkowsky (9) found that sodium resinate may be hydrolyzed as much as sixty percent in the beater, depending upon the pulp used. He attributes the hydrolysis to the alkali removal by the pulp, and shows that the purer pulps remove less alkali than the more impure pulps.

**COLLOIDAL THEORIES**

Schwalbe (50) advances the theory that ink fastness of resin sized paper is due to the precipitation of mixtures of Al(OH)3 and free resin; the function of the Al(OH)3 is to inclose the particles of resin and prevent deterioration of sizing due to atmospheric oxidation. The Al(OH)3 also prevents the resin particles from flowing together in the drying cylinders. Schwalbe and Robechn (52) claim that Al(OH)3 is of considerable importance in sizing and that a greater part of the alumina is fixed on the fibers not combined with the resin. Stockigt and Kinger (55) say that it is possible to size paper with colloidal resin, but only by the use of aluminum sulfate as the electrolyte, the sizing appearing to take place in two steps: (a) formation of
adsorption compounds of resin, and Al(OM)$_3$; (b) adsorption of this colloidal phase by the fibers.

Reiner (26) differs with Stockigt and Klinger in that he claims that colloidal cellulose attracts the colloidal aluminum hydrate, leaving the cellulose positively charged. The fibers then adsorb the negatively charged resin sol, resulting in sized paper. Lorenz (34) maintains that all sizes are colloidal and that due to the large dilution in the beater, complete hydrolysis takes place, setting resin acid free, this condensing to form colloidal particles. He believes that chemical reactions such as the formation of aluminum resinate cannot occur under these conditions; since resin acids and resinate ions are only present in small amounts. He suggests that alum acts as a coagulating medium and not as a chemical agent. Accordingly, with negatively charged cellulose and negatively charged resin sols in intimate contact, such as would occur in the beater, the paper can be sized; but the film cracks and breaks down on aging, permitting ink to penetrate the fibers. With Al(OM)$_3$ the cellulose and resin would be bonded together resulting in a permanently sized paper.

Studies by Ostwald and Lorenz (43) led to the following conclusions:
(1) Al$_2$(SO$_4$)$_3$ and sodium resinate are greatly hydrolyzed in the beater;
(2) the greater the valence of the cation, the greater the flocculating action of electrolytes on the abietic acid hydrosol. Cellulose is electronegative, alum treated fibers are positive and colloidal resin is negatively charged. The positively charged alumina is absorbed by the fibrous interfaces of the negatively charged cellulose fibers.
Alumina also forms a positive layer around the electronegative resin particles, so that the colloidal alumina acts as an electrostatic binding material between the fiber and resin. Thiriot and Delcroix (60) confirm the work of Ostwald and Lorens as to the mechanism of resin sizing. Over a certain range of pH, the cellulose and resin have electric charges of opposite signs so that the positively charged resin and the negatively charged cellulose are mutually attracted and sizing is possible. Cenni (39) suggests that the theory, as outlined by Lorens, is the more logical one to explain why different amounts of alum are necessary in different mills to produce the same sizing results. He also notes that other metals, such as chromium, iron, copper, and zinc, may be substituted for aluminum. In the same paper he also points out that the aluminum in the sizing bath acts as a mordant for the free resin.

Arnott (4) examined sized and un sized fibers under the microscope and from observations he suggests that the alumina is deposited on the resin particles.

Roosdier (46) found that the maximum adsorption of fillers in papers occurs at pH of 5.6 and remains constant from 5.6 to 7.0. He claims that the figure is no doubt closely related to the maximum adsorption of resin by fibers. Olsen and Gortner (42) claim that resin is adsorbed by the fibers and that the amount of adsorption depends upon the nature of the fibers to a large extent.

Stroehm (56) believes that there is a formation in the fibers of a semi-permeable membrane of alumina which prevents diffusion of resin into the fiber and that positively charged alumina is adsorbed in the
negative fiber surface and in turn adsorbs negative resin, thus forming a bond between the resin and the fiber surface. This theory does not, however, preclude the formation of aluminum resinate.

Kamimura (30) has made a detailed study of the effects of zeta potential of the cellulose fibers on the sizing process. His results indicate that sizing efficiency depends upon the quality and nature of the pulp and that a decidedly negative pulp has, in general, a better sizing efficacy. He studied the potential difference existing at the fiber interface. As both fiber and resin are negatively charged very little resin is fixed in the absence of alum. Addition of alum results in the fixation of the resin - Al(OH)₃ aggregate.

Kamimura and Tanahata studied the effect of potassium, sodium, magnesium, and alumina chlorides, potassium and aluminum sulfates, HCl, H₂SO₄, NaOH and TH(PO₃)₃ on the charge of particles in the hydrocols of acetic acid and its sodium soap and upon the turbidity of these sols. The charge was calculated from the electro-phoretic velocity of particles by ultra microscopical examination using non-polarizing electrodes. They found that Al₂(OH)₃ lowers the interfacial potential of both the fibers and resin particles nearly to a certain low value and weakens the mutual repulsive force.

HATING AND HEATING

Klemm (32) finds that engine sized papers are not fully ink resistant if dried at too high or too low a temperature. He considers
80° C. about right. This temperature must be reached while the sheet is still wet, as dry resin does not melt at as low a temperature as when moist. The first dryer should not be too hot, then raise the temperature of the paper rapidly to 80° C. and gradually lower it to the end of the bank. In a later paper Klemm (33) says that fritting (incipient fusion) takes place at 70° - 80° C. and before the moisture content of the sheet falls below fifty percent and forms a continuous im pervious film. Heuser (86) states that the last step in sizing is sintering on the driers at a temperature of 70° - 80° C. before the moisture content falls below fifty percent. Hinton (35) found that a temperature of 30° C. would not develop sizing in paper made from well sized stock but that 77° C. gave good results. Minor (33) states that paper taken from the machine before reaching the driers and then air dried is usually poorly sized as compared with that which is dried as usual. He adds that if the amount of alum is insufficient the sizing is not increased by the heat of the driers.

Heilmann (25) points out that poorly sized paper, to which enough resin size has originally been added to size it well, is greatly improved when heated for a minute at 105° C. Schwalbe (53) studied the effect of heating on sizing. One specimen gave a sizing test of 280 seconds as it came from the machine; 866 seconds after pressing with a flat iron at a temperature of 95° to 100° C. and 6940 seconds at a temperature of 250° C. An anonymous writer (2) states that poorly sized paper can be made well sized by dampening and rapidly drying at 110° C. while
unstretched.

Hare (15) studied the effect of temperature on sizing but found no sudden change at the melting point of the resin. Osman (40) found that strong heating of the moist paper sheet is detrimental to sizing. He found that if resin sized paper with a moisture content of 65 percent or more is warmed to 75° C. for one minute the degree of sizing is greatly decreased or even destroyed. Harrison (23) confirms Osman’s statement that the relation between moisture content and drying temperature is an obscure one. The results of tests on air dried sheets indicate that a high drying temperature is not always essential for the development of sizing.

G. W. (20) found that for a neutral size it made no difference whether the paper had been air dried or cylinder dried but when a high free resin size was used, the size tests were increased by having the paper cylinder dried.

ROBIN DETERMINATIONS AND SIZE TESTS

Croswell, Freshfield, and Keller (13) found that laboratory hand sheets retained around 90 percent of the size added as compared to 30-90 percent retention in mill runs. This difference is attributed to the high dilution of the stock in making the hand sheets.

Hare (15) states that the resin content of the paper does not necessarily bear any relation to its sizing.
Sutermeister and Torrey (39) find that the usual extraction of paper with alcohol acidified with acetic acid will not remove all the resin, nor will this treatment followed by extraction with ether. If sulfuric acid is used in place of acetic, practically complete extraction is obtained but it is necessary to siphon the solvent many more times than the twelve times recommended in the standard method. Olen and Gortner (42) found that a neutral ether extract does not remove all the resin adsorbed since subsequent extraction with acidified alcohol yields a resin-like material which is soluble in ether. They claim that it is not a case of solubility but suggest that the charge of the fibers must be neutralized so as to release the resin particles.

From a study of thirty-eight methods, Carson (12) concludes that the dry indicator method and the curl method gives the most consistent and dependable values for the degree of internal sizing. Alexander (1) studied the Valley tester and found that its results were greatly influenced by the furnish and formation of the sheet. He found no relation between the Valley test and the ink flotation test and concluded that the Valley tester could not be used for comparing the sizing qualities of different grades of paper.
CHAPTER III.

PRESENTATION OF PROBLEM

In the sizing of paper in the beater, a very complicated system is set up consisting of pulp fibers, water, resin size, alum, and all the impurities normally present with each of these materials. Since sodium resinate is the salt of a strong base and a weak acid and aluminum sulfate is the salt of a weak base and a strong acid and both are in a highly diluted state in the beater, a certain amount of hydrolysis is expected. On hydrolysis free colloidal resin and alumina would be formed and as these two substances are highly insoluble in water there could be no aluminum resinate formed. Hence, if aluminum resinate is formed, it must be derived from the reaction between sodium resinate and aluminum sulfate. The aluminum resinate, in contrast to a resin-alumina aggregate, should have a definite chemical composition and show definite solubility properties. Needle and Nolan (7) and Blalkowsky (9) found that sodium adipate undergoes very little hydrolysis at beater concentrations while Haug (26) and Ivanov (29) claim that the sodium soap undergoes complete hydrolysis at dilutions existing in the beater. However, Blalkowsky (9) showed that cellulose fibers played an important role in the sizing mechanism, due to their ability to reduce the alkalinity of the sodium resinate with the resulting formation of free colloidal resin. Since Blalkowsky (9) has established that dilute sodium resinate solutions undergo hydrolysis in the presence of pulp fibers but
but fail to do so in their absence, a relatively larger amount of free resin and smaller amount of aluminum resinate is to be expected on the addition of aluminum sulfate in the presence of pulp fibers than in their absence. The relative amounts of aluminum resinate and free resin found in the resin-alum precipitate is, therefore, a clue to the mechanism involved in the sizing reaction as well as a measure of the degree of hydrolysis of the sodium resinate as it exists in the beater. This particular report deals first with a study of the properties of the precipitate obtained on the addition of aluminum sulfate to dilute sodium abietate solutions in order to develop an analytical method for studying the sizing mechanism; secondly, with an investigation of the reaction between an excess of aluminum sulfate and dilute solutions of sodium abietate in distilled water in the absence and presence of pulp fibers by means of the method developed; thirdly, with a determination of the relative ease of sizing of various pulp fibers, employing beater runs, in relation to their behavior toward sodium abietate and aluminum sulfate; and fourthly, with the effect of such variables as drying temperature and resin retention on the sizability of a given pulp.
CHAPTER IV.

EXPERIMENTAL DISCUSSION

A. PROPERTIES OF THE PRECIPITATE FORMED ON THE ADDITION OF AN EXCESS OF ALUMINUM SULFATE TO DILUTED SODIUM ABIETATE SOLUTIONS AND DEVELOPMENT OF AN ANALYTICAL PROCEDURE.

1. MATERIALS

Preparation of Abietic Acid: Six hundred grams of commercial abietic acid was refluxed for one hour with 96 percent acetic acid. The mixture was filtered, cooled, and allowed to crystallize. The crystals were filtered as dry as possible on a Buchner funnel using suction. The crystals were then washed with successive portions of cold 85 percent ethyl alcohol. The abietic acid was then twice crystallized from absolute ethyl alcohol and air dried. The acid number was determined by dissolving exactly one gram of abietic acid in 125 cc of 95 percent ethyl alcohol and titrating with standard N/10 sodium hydroxide solution using phenolphthalein as an indicator. The acid value found was 131.9 as compared to the theoretical acid value of 132.4 assuming a monobasic acid.

Preparation of a Standard Sodium Abietate Solution: A N/10 solution of sodium abietate was prepared by dissolving 30.33 grams of abietic acid in 50.5 cc of 0.1975 N. NaOH and then diluting to exactly one liter. A clear straw yellow solution was obtained. Solutions of lower concentrations were made from this standard solution by careful dilution.
Distilled water essentially free from carbon dioxide was used throughout.

**Preparation of a Standard Aluminum Sulfate Solution**: A N/10 solution of aluminum sulfate was prepared by dissolving 57.02 grams of C.P. aluminum sulfate in carbon dioxide free distilled water and diluted to exactly one liter.

**Preparation of Pulp Samples**: The various pulps as obtained from the mills were torn up into small pieces, sampled and air dried. The pulps were then disintegrated in the Gesta pulp disintegrator and placed in stoppered containers.

2. **METHOD OF PROCEDURE AND DATA**

One hundred c.c. of a N/10 sodium acetate solution was precipitated with three times the theoretical amount of aluminum sulfate. This should give 0.3102 grams of aluminum acetate if no hydrolysis has taken place and all of the sodium acetate is converted into the aluminum soap; the precipitate was dried in a vacuum oven at 50° C. and extracted with benzene and filtered.

Weight of extractive No. 1 = 0.3118
Weight of extractive No. 2 = 0.3123

Additional precipitations were carried out under the above conditions and the aluminum acetate dried under the above conditions was found to be soluble in benzene, chloroform, and absolute ether.
but insoluble in absolute alcohol and acetone. Abietic acid was found to be soluble in alcohol, benzene, chloroform, and ether. If the aluminum abietate was dissolved in commercial ether containing small amounts of water, part of the aluminum abietate settled out on standing. On ashing the evaporated and weighed benzene extract, it was found that the $\text{Al}_2\text{O}_3$ content was in fair agreement with the $\text{Al}_2\text{O}_3$ content demanded by the formula $\text{Al}(\text{C}_9\text{H}_{16}\text{O}_2\text{O}_6)$.

Weight of benzene extract No. 1 = 0.3143 g.
Weight of benzene extract No. 2 = 0.3206 g.

Weight of Ash ($\text{Al}_2\text{O}_3$) in No. 1 = 0.0166 g.
Weight of Ash ($\text{Al}_2\text{O}_3$) in No. 2 = 0.0173 g.

Percent $\text{Al}_2\text{O}_3$ in No. 1 = 5.37 %
Percent $\text{Al}_2\text{O}_3$ in No. 2 = 5.40 %

The theoretical percentage of $\text{Al}_2\text{O}_3$ is 5.49 %.

When the wet filtered precipitates were dried in an electric oven at 80° C, the aluminum abietate which was originally white in color turned brown and exhibited different properties than that of the aluminum soap dried at 50° C. in a vacuum oven. It was found that only part of the precipitate was now soluble in benzene. Boiling the insoluble portion in benzene did not increase the solubility.

Weight of precipitate No. 1 Soluble in benzene = 0.1953 g.
Weight of precipitate No. 2 Soluble in benzene = 0.1611 g.
Percent of precipitate No. 1 Soluble in benzene = 52.6 %
Percent of precipitate No. 2 Soluble in benzene = 51.6 %

Average percent Ash (Al₂O₃) in soluble portion = 2.85 %
Average percent Ash (Al₂O₃) in insoluble portion = 9.15 %

Commercial samples of paper were obtained that had gone through
the press sections; these were air dried and extracted with chloroform
and the extract ashed. Papers were obtained made under the same condi-
tions except that these had gone through the driers. These were also
extracted with chloroform evaporated and ashed. The resin size used
contained 60 % free resin.

Percent resin in air dried paper as extracted
with chloroform = 1.15 %
Percent resin in paper that had gone through
the drier sections = 0.82 %

Percent Ash (Al₂O₃) in air dried paper = 2.35 %
Percent Ash (Al₂O₃) in machine dried paper = 1.69 %

A 1:100 sodium abietate solution was precipitated with an
excess of aluminum sulfate in the presence of pulp fibers. After filter-
ing the fibers on a Buchner funnel using suction, the pad was dried in
a vacuum oven at 50° C. and then extracted for six hours in a Soxhlet,
using benzene. At the end of this time it was observed that the benzene
solution was quite turbid and that part of the aluminum abietate had
precipitated out, due to decomposition in the boiling benzene solution.
When this same procedure was repeated with chloroform, the solution was quite clear and on weighing the extract it was found that all of the resin added to the pulp had been extracted. The lower boiling point chloroform did not decompose the aluminum abietate in the extraction process.

II. DISCUSSION

On precipitating a dilute sodium abietate solution with an excess of aluminum sulfate, a white gelatinous precipitate is obtained. When this precipitate is dried at 50° C. in a vacuum oven, it is completely soluble in benzene, chloroform, and absolute ether and insoluble in absolute alcohol and acetone. If the precipitate is dissolved in benzene and the solution filtered through a fritted glass crucible to remove traces of occluded aluminum sulfate, evaporated and analyzed for the aluminum oxide content, it is found that the percent Al₂O₃ is in fair agreement with an alumina content demanded by a neutral aluminum abietate Al(O₁₉H₂₅COO)₃. This would be the result of a reaction taking place as follows:

$$6O_{19}H_{25}COONa + Al_2( SO_4)_3 \rightarrow 3Na_2SO_4 + 2Al(O_{19}H_{25}COO)_3$$

However, if the precipitate is dried at 80° C., it turns brown and undergoes a certain amount of decomposition. The decomposition products can be divided into two parts; one of these is soluble in benzene, chloroform, and ether, and on analysis is found to have a lower Al₂O₃ content than the neutral aluminum.
achitate; the second portion is insoluble in these solvents and has a higher \( \text{Al}_2\text{O}_3 \) content than the neutral aluminum soap. Schön and Kludtis (19) suggest that the following reactions take place at a temperature of 105° C. in the presence of moisture:

1. \( \text{Al}(\text{OH})(\text{C}_1\text{H}_2\text{O}_2\text{COO})_2 \rightarrow \text{Al}(\text{OH})(\text{C}_1\text{H}_2\text{O}_2\text{COO})_2 + \text{C}_1\text{H}_2\text{O}_2\text{COOH} \)

2. \( \text{Al}(\text{OH})(\text{C}_1\text{H}_2\text{O}_2\text{COO})_2 + 2\text{H}_2\text{O} \rightarrow \text{Al}(\text{OH})(\text{C}_1\text{H}_2\text{O}_2\text{COO}) + 2\text{CO}_2 \)

The percentage of \( \text{Al}_2\text{O}_3 \) in \( \text{Al}(\text{OH})(\text{C}_1\text{H}_2\text{O}_2\text{COO})_2 \) is 7.11% and in \( \text{Al}(\text{OH})(\text{C}_1\text{H}_2\text{O}_2\text{COO}) \) is 14.07%. Both of these basic achitates are insoluble in benzene, chloroform, and ether. Since, in this investigation, it was found that approximately half of the aluminum achitate was converted into an insoluble portion having an average \( \text{Al}_2\text{O}_3 \) content of 9.15%, it is probable that this portion may be a mixture of the two aluminum achitates as formed in the above reactions. Since the soluble portion had an average \( \text{Al}_2\text{O}_3 \) content of 2.85 percent it is probable that it consists of a mixture of free achetic acid and neutral aluminum achitate. We should expect this same decomposition to take place at least in a portion of the aluminum resinate present in commercial paper as the wet web passes over the dryer. Air dried paper was extracted with chloroform, evaporated, dried, weighed, ignited,ashed, and weighed, and it was found that the resin content and \( \text{Al}_2\text{O}_3 \) content of the resin was greater than in the same paper that had gone through the dryer. This substantiates the work of certain investigators who claim that aluminum resinate formed in the beater is decomposed on the dryer rolls.
When chloroform was used for extracting sized paper that had been dried at a low temperature or air dried, all of the resin was extracted and no decomposition took place in the extraction flask.

When benzene was used, some of the aluminum resinate extracted from the paper was decomposed into an insoluble portion in the boiling benzene. Olsen and Germer (42) stated that all of the resin could not be extracted from pulp fibers by means of a neutral solvent such as ether because the resin particles were electrically charged; they claimed that an acidified alcohol solution was needed to neutralize this charge.

The work carried out in this investigation indicates that a neutral solvent can be used to remove all the resin providing the solvent is free of moisture and the resin precipitate dried at a sufficiently low temperature or air dried. However, a neutral solvent cannot be used for commercial papers that have passed through the dryer sections.

The method of procedure as adopted includes: 1. drying the resin precipitate, in the absence and presence of pulp, at 50°C in a vacuum oven; 2. extracting the resin precipitate with benzene and in the presence of fibers with chloroform; 3. determining the total weight of resin by evaporation of the chloroform and the Al2O3 content by ignition of the extract; and 4. calculating the amount of free and combined resin present.
B. EFFECT OF LOWERS ALUMINUM SULFATE ON DIURETIC SODIUM DEPENDENT SOLUTIONS IN THE ABSENCE AND PRESENCE OF PURINE NUCLEOTIDES.

1. METHOD OF PROCEDURES

Standard purified sodium acetate solutions, 0.0100N, 0.0075N, 0.0050N, and 0.0025N were made up by the proper dilution of the 1/10 sodium acetate solution with carbon dioxide-free water. Wilmot flask of 500 c.c. capacity containing 250 c.c. of each of these solutions were placed in a bath of 20°C. Three times the theoretical amount of aluminum sulfate was then added to each solution and the contents were allowed to stand for two hours in the bath with occasional shaking by hand. The precipitate was then filtered by means of suction and dried in a vacuum oven at 50°C.; pH measurements were made on the filtrate by means of the LaMotte colorimeter method. The dried precipitate was then dissolved in benzene and filtered through a fritted glass crucible using suction. The benzene solution was transferred to a weighed platinum dish; the suction flask was rinsed once or twice with benzene and added to the dish. The benzene solution was then evaporated to dryness on an electric hot plate placed under a hood. After evaporation, the dish and contents were placed in an electric drying oven at 75°C. and dried to constant weight. The dish and contents after weighing were carefully ignited over a small gas flame and then ashed in a muffle furnace to constant weight. Duplicate runs were made in all cases.
The following procedure was adopted for carrying out the above reaction in the presence of pulp fibers. Sufficient air dried disintegrated pulp to make ten grams of bone dry stock was placed in a 500 c.c. Erlenmeyer and 150 c.c. of this standard 0.0100N, 0.0050N, or 0.0025N sodium bisulfite solution added. The pulp and sodium bisulfite were well mixed and allowed to remain in a bath at 20° C. for twenty-four hours. At the end of this time, sufficient aluminum sulfate was added to give approximately the same pH as was obtained in the absence of fibers. The flask and contents were well shaken and allowed to stand in a bath at 20° C. for two hours. The fibers were then filtered on a Buchner funnel using suction; the filtrate was poured repeatedly through the fiber pad formed until it became perfectly clear. The pad was removed from the funnel, broken up into small pieces by hand, placed on a large watch glass and dried at 50° C. in a vacuum oven. The dried fibers were then placed in a fat free extraction thimble and extracted for six hours in a Soxhlet extractor, with chloroform. The chloroform in the extraction flask was then transferred to a weighed platinum dish and evaporated to dryness on an electric hot plate. The platinum dish and contents were then dried in an electric oven at 75° C. to constant weight. The resin was then ignited over a small gas flame and then ashed to constant weight in a muffle furnace. Duplicate runs were made in all cases. Samples of pulp were extracted with chloroform to determine the amount of extractives originally present in the pulp.
2. CALCULATIONS

The following is a sample of the calculations made in compiling Tables I and II on pages 34, 35, 37, 38, and 39.

Weight of dish + extract = 21.2733 g.
Weight of dish = 20.6629 g.
Total extract = 0.6104 g.

Total extract = 0.3076 g.
Pulp blank extract = 0.0639 g.
Al\((\text{O}_{12}\text{H}_{23}\text{O}_{20})\)\(_3 + \text{O}_{12}\text{H}_{20}\text{O}\)\(_{20}\) = 0.3213 g.

Weight of dish + ash = 20.8545 g.
Weight of dish = 20.6629 g.
Weight of Ash (Al\(_2\text{O}_3\)) = 0.1916 g.

Percent Al\(_2\text{O}_3\) = \(\frac{0.1916}{0.3219}\) (100) = 6.06%.

Weight of Al\((\text{O}_{12}\text{H}_{23}\text{O}_{20})\)\(_3\) = (0.01880)(10.27) = 0.3935 g.

Weight of Al\((\text{O}_{12}\text{H}_{23}\text{O}_{20})\)\(_3 + \text{O}_{12}\text{H}_{20}\text{O}\)\(_{20}\) = 0.3439 g.
Weight of Al\((\text{O}_{12}\text{H}_{23}\text{O}_{20})\)\(_2 + \text{O}_{12}\text{H}_{20}\text{O}\)\(_{20}\) = 0.1839 g.
Weight of free \(\text{O}_{12}\text{H}_{20}\text{O}\)\(_{20}\) = 0.0539 g.

Percent of Al\((\text{O}_{12}\text{H}_{23}\text{O}_{20})\)\(_3\) based on weight of extract = \(\frac{0.3439}{0.3919}\) (100) = 87.9%.

Percent of free \(\text{O}_{12}\text{H}_{20}\text{O}\)\(_{20}\) based on weight of extract = 100.0 - 87.9 = 12.1%.

Percent of free \(\text{O}_{12}\text{H}_{20}\text{O}\)\(_{20}\) based on bone dry weight of pulp = \(\frac{0.0535}{10.000}\) (100) = 0.35%.
Percent Al(13.29 g)_{2} based on bone try weight of pulp = \frac{0.3439}{10.000} \times 100 = 3.44% 

3. DATA

Table I gives the results as to the composition of the precipitate obtained when three times the theoretical amount of aluminum sulfate is added to 250 c.c. of the various sodium acetate solutions.
| Normality of Sodium Sulphate | Weight of sodium sulphate (g) | Weight of alumino silicate ash (g) | Percent of sodium sulphate in the ash (g) | Percent of free alumino silicate (g) | Effect of free alumino silicate on pH of all solutions
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An excess over the theoretical amount of aluminum sulfate necessary to give the same pH as in Table I, page 78, in the absence of pulp was added to pulp suspensions in the dilute sodium acetate solutions. Table II shows the results obtained on the composition of the precipitate, and the effect of the pulp fibers on its composition.
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<th>Percent H₂SO₄ on basis of pulp</th>
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<th>Weight of ash (gms)</th>
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<th>Percent MgCO₃ based on extract</th>
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<td>Percent H₂SO₄ on basis of pulp</td>
<td>Percent Al₂(OH)₃ on basis of pulp</td>
<td>Weight of extract gms.</td>
<td>Weight of extract corrected gms.</td>
<td>Weight of ash gms.</td>
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**TABLE II (Continued).**

EFFECT OF EXCESS ALUMINUM SULFATE ON DIURESIS.  
SODIUM AMINOSULFATE SOLUTIONS IN THE PRESENCE OF VARIOUS PULPS.
TABLE II (Continued).

EFFECT OF EXCESS ALUMINUM SULFATE ON DIURNAL SODIUM AMERATE SOLUTIONS IN THE PRESENCE OF VARIOUS PULPS

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<th>Percent NaAl(OH)₃ on basis of pulp</th>
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<th>Weight of ash gm.</th>
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<td>Blank</td>
<td>Semi ML Kraft</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure No. 1
Effect of Excess Aluminum Sulphate on Dilute Sodium Ablate Solutions in the Presence of Pulp Fibers
Time: 24 Hours
Temperature: 20°C
pH: 4.2
1) Unbleached Mitscherlich
2) Alpha
Figure No II
Effect of Excess Aluminum Sulfate on Dilute Sodium Albitate Solutions in the Presence of Pulp Fibers
Time: 24 Hours
Temperature: 20°C
pH: 4.2
1) Unbeached Mitscherlich
2) Alpha

Percent Resin Added As Soap
5. DISCUSSION.

Table I, page 34, indicates that sodium abiate solutions at concentrations existing in the beater give only the normal aluminum abiate when precipitated with sufficient excess of aluminum sulfate to produce a pH that approximates that of a hard sized stock going over the machine. This confirms the work of Schutz and Klendt (45); they found that only the neutral aluminum soap was formed even when twelve times the theoretical amount of aluminum sulfate was used in precipitating the sodium abiate. The sodium abiate cannot be hydrolyzed to any extent and at the same time react to form only the aluminum soap. If the sodium abiate at beater concentrations is hydrolyzed completely, as is claimed by Enns (24) and Ivanov (23), then no aluminum abiate could be formed since the insoluble colloidal free resin would only be coagulated by the aluminum sulfate. The results obtained in this investigation indicate that in the absence of pulp fibers the sodium abiate is very little hydrolyzed and that only the normal aluminum abiate is formed on the addition of aluminum sulfate.

Eight different pulps at consistencies of four percent in the presence of three different concentrations of sodium abiate corresponding to 1.90, 3.79, and 7.56 percent abiotic acid on the bone dry basis of the pulp were treated with an excess of aluminum sulfate. Data in Table II, pages 36, 37, 38, and 39 shows that more aluminum sulfate was needed to produce the same pH in the presence of pulp than in the absence of pulp.
fibers. This was found to be especially true at the two lower concent-
trations of sodium abietate. The two kraft pulps required more aluminum
sulfate than the other pulps. The pulps were allowed to stand in contact
with the sodium abietate solutions for twenty-four hours at 20° C. before
adding the aluminum sulfate, in order to determine the effect of the pulp
fibers. Balzowsky (9) found that dilute sodium abietate solutions were
hydrolyzed as much as sixty percent when allowed to stand in contact with
pulp fibers. He found that the amount of hydrolysis depended upon the
pulp used and attributed this phenomena to

\[
\text{Pulp} + H_2SO_4 \rightarrow \text{Fibers} + H_2O + C_{17}H_{29}O_8 \text{SO}_4
\]

the ability of the cellulose fibers to reduce the alkalinity of the solu-
tion and force the hydrolysis of the sodium soap, thereby liberating
colloidal free resin. Since we could not expect a chemical reaction to
take place between any liberated colloidal abietic acid and aluminum sul-
fate, the amount of aluminum abietate formed would be dependent upon the
amount of the resin still in the combined form as the sodium soap; the
amount of free resin formed would be dependent upon the degree to which
the pulp fibers forced the hydrolysis of the sodium abietate. By extract-
ing the resin precipitates from the pulp fibers with chloroform and
evaporating andashing the resin, the amount of Al₂O₃ can be determined.
If the resin extract is corrected for the extract originally present in
the pulp and converting the Al₂O₃ content found to aluminum abietate,
the amount of free resin can be calculated (page 32 on Calculations).
From this data obtained, it can be seen that the pulp fibers force the
hydrolysis of sodium abietate to some extent, and that free resin as well as aluminum resinate is formed as a result of this hydrolysis; the amount of free resin obtained varies with the concentration of sodium abietate and the pulp used. Curves on pages 30 and 41 show the effect of two pulps on three different concentrations of sodium abietate when allowed to stand in contact with the soap for twenty-four hours and then precipitated with an excess of aluminum sulfate. Since pulps alter the equilibria of sodium abietate and different pulps behave differently in the amount to which they change this equilibria, no two systems can be expected to be the same when pulp fibers are sized in the beater.

3. THE RELATIVE BASE OF SIZING OF VARIOUS PULPES IN RELATION TO THEIR BEHAVIOR TOWARD SODIUM ABIEATE AND ALUMINUM SULFATE.

1. METHOD OF PROCEDURE.

Beefer runs were made with the eight different pulps, duplicating as nearly as possible the system set up in studying the resin precipitate in the presence of the various pulps, as shown in Tables I and II, pages 34, 36, 37, 38, and 39. The pulps were soaked in distilled water for forty-five minutes and then added to the beater and slushed for five minutes. The weights were then added to the lever arm and the pulps were beaten at a consistency of two percent in distilled water. Two percent sodium abietate on the bone dry basis of the stock was added to the beater at the beginning of the run. The stocks were all beaten to approximately the same freeness. The weights were removed
and sufficient C.P. Al₂(3OH)₃ • 18H₂O was then added to give a pH of 4.5. The stock was then allowed around for five minutes to insure good mixing. Hand sheets were made to weigh approximately 36 pounds on the 24 x 36 x 1/30 basis. The sheets were all made under identical conditions; they were all made at the same consistency, pressed at 100 pounds per square inch for one minute, and dried in an electric dryer for exactly ten minutes at 105° C. All of the sheets, before testing, were conditioned in the humidity room at 65 degrees relative humidity and 70° F. The sheets were trimmed down to 5 x 5 inches, thickness measured, basic weight taken, porosity measurements made and the Valley, Currier-Caron curl and dry indicator tests made on the various sheets. Duplicate beater runs were made on the same eight pulps under exactly the same conditions except that tap water, commercial rosin size (30% free) and paper makers' alum were used. The sheets were tested under the same conditions as in the above procedure. The data as shown in Tables III, IV, V, VI, VII, VIII, IX are average values obtained by testing a large number of samples.

2. TESTS AND APPARATUS.

Size tests were made on hand sheets by means of the Valley size tester, the Currier size tester, the Caron curl size tester, and by means of the dry indicator method as described in T.A.P.P.I. standards. Porosity measurements were made with the Gurley densimeter. The hydrogen ion concentrations were measured by means of the LaBette
colorimetric pH set. Schlot extractor with ground glass joints were used for all extraction work. The samples were placed in extraction thimbles that were fat free. Platinae dishes were used for all evaporations and ignitions, and an electric muffle furnace was used for ashing. Beater runs were made in a one pound Valley Iron Works beater and the hand sheets were dried in a Williams electric dryer controlled at 105° C.

3. DATA.

Beater runs were made in distilled water with eight different pulps to determine their relative ease of sizeability when made under the same conditions. Two percent sodium acetate and sufficient alum to produce a pH of 4.5 were used. Four different size tests were made on samples of hand sheets. Table III gives the results of size tests as well as other tests made on the hand sheets.
### TABLE III.

**RELATIVE SIZABILITY OF VARIOUS PULPS**

<table>
<thead>
<tr>
<th>Type of pulp</th>
<th>Final pulp</th>
<th>Tenseness</th>
<th>Weight 3&quot;x5&quot; sheet gms.</th>
<th>Thickness inches</th>
<th>Permeability 100 c.c. sec.</th>
<th>Valley test sec.</th>
<th>Carrier test sec.</th>
<th>Dry indicator test sec.</th>
<th>Carry curl sec.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Groundwood</td>
<td>360</td>
<td>0.86</td>
<td>0.0052</td>
<td></td>
<td>16</td>
<td>42</td>
<td>102</td>
<td>32</td>
<td>11</td>
</tr>
<tr>
<td>Unbl. Kraft</td>
<td>370</td>
<td>1.14</td>
<td>0.0042</td>
<td></td>
<td>214</td>
<td>21</td>
<td>45</td>
<td>67</td>
<td>26</td>
</tr>
<tr>
<td>Unbl. Kitch.</td>
<td>390</td>
<td>1.04</td>
<td>0.0037</td>
<td></td>
<td>162</td>
<td>14</td>
<td>26</td>
<td>44</td>
<td>29</td>
</tr>
<tr>
<td>Unbl. Sulfite</td>
<td>385</td>
<td>0.94</td>
<td>0.0031</td>
<td></td>
<td>183</td>
<td>13</td>
<td>19</td>
<td>62</td>
<td>15</td>
</tr>
<tr>
<td>Semi Bl.Kraft</td>
<td>370</td>
<td>1.05</td>
<td>0.0036</td>
<td></td>
<td>206</td>
<td>21</td>
<td>50</td>
<td>75</td>
<td>42</td>
</tr>
<tr>
<td>Bached Sulfite</td>
<td>360</td>
<td>1.05</td>
<td>0.0035</td>
<td></td>
<td>206</td>
<td>21</td>
<td>50</td>
<td>75</td>
<td>42</td>
</tr>
<tr>
<td>Alpha</td>
<td>390</td>
<td>1.02</td>
<td>0.0039</td>
<td></td>
<td>81</td>
<td>15</td>
<td>29</td>
<td>46</td>
<td>25</td>
</tr>
<tr>
<td>Rag</td>
<td>370</td>
<td>1.04</td>
<td>0.0044</td>
<td></td>
<td>75</td>
<td>4</td>
<td>7</td>
<td>15</td>
<td>10</td>
</tr>
</tbody>
</table>
Size tests listed in Table IV indicate the relative ease of sizing various pulps. The beater runs were made in tap water under the same conditions. Two percent resin size (30% free) and sufficient alum to produce a pH of 4.5 were used. Three different size tests were made on samples of hand sheets.
<table>
<thead>
<tr>
<th>Type of pulp</th>
<th>Final pulp freeeness</th>
<th>Weight 5&quot; x 5&quot; sheet gm.</th>
<th>Thickness inches</th>
<th>Porosity 100 c.c. sec.</th>
<th>Valley size sec.</th>
<th>Currier size sec.</th>
<th>Dry indicator test sec.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Groundwood</td>
<td>200</td>
<td>0.76</td>
<td>0.0063</td>
<td>9</td>
<td>25</td>
<td>96</td>
<td>34</td>
</tr>
<tr>
<td>Ubl. Kraft</td>
<td>290</td>
<td>1.08</td>
<td>0.0040</td>
<td>167</td>
<td>17</td>
<td>34</td>
<td>99</td>
</tr>
<tr>
<td>Ubl. Misch.</td>
<td>320</td>
<td>1.53</td>
<td>0.0042</td>
<td>220</td>
<td>12</td>
<td>31</td>
<td>95</td>
</tr>
<tr>
<td>Ubl. Sulfite</td>
<td>340</td>
<td>0.95</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Semi H. Kraft</td>
<td>330</td>
<td>0.91</td>
<td>0.0034</td>
<td>77</td>
<td>14</td>
<td>30</td>
<td>41</td>
</tr>
<tr>
<td>Mashed Sulfite</td>
<td>290</td>
<td>1.02</td>
<td>0.0033</td>
<td>155</td>
<td>13</td>
<td>33</td>
<td>57</td>
</tr>
<tr>
<td>Alpha</td>
<td>350</td>
<td>0.96</td>
<td>0.0037</td>
<td>96</td>
<td>16</td>
<td>34</td>
<td>42</td>
</tr>
<tr>
<td>Bag</td>
<td>240</td>
<td>0.94</td>
<td>0.0036</td>
<td>113</td>
<td>5</td>
<td>35</td>
<td>33</td>
</tr>
</tbody>
</table>
Table V compares the percent of sodium abietate hydrolysed as obtained in Table II, pages 36, 37, 38, and 39, with the size tests of the various pulps as obtained in Table III, page 47.
TABLE V.

EFFECT OF PINE RESIN ON SIZE TESTS OF VARIOUS PULPS.

<table>
<thead>
<tr>
<th>Type of pulp</th>
<th>Valley size test sec.</th>
<th>Carrier size test sec.</th>
<th>Dry indicator size test sec.</th>
<th>Gesen curl test sec.</th>
<th>Percent NaOH Hydrolysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Groundwood</td>
<td>42</td>
<td>101</td>
<td>32</td>
<td>11</td>
<td>4.6</td>
</tr>
<tr>
<td>Ubl. Kraft</td>
<td>21</td>
<td>45</td>
<td>67</td>
<td>26</td>
<td>24.4</td>
</tr>
<tr>
<td>Ubl. Hitech</td>
<td>14</td>
<td>26</td>
<td>44</td>
<td>29</td>
<td>32.6</td>
</tr>
<tr>
<td>Ubl. Sulfite</td>
<td>13</td>
<td>19</td>
<td>62</td>
<td>15</td>
<td>23.5</td>
</tr>
<tr>
<td>Semi Bl. Kraft</td>
<td>21</td>
<td>50</td>
<td>75</td>
<td>42</td>
<td>44.0</td>
</tr>
<tr>
<td>Bleached Sulfite</td>
<td>15</td>
<td>29</td>
<td>46</td>
<td>25</td>
<td>17.2</td>
</tr>
<tr>
<td>Alpha</td>
<td>18</td>
<td>31</td>
<td>43</td>
<td>20</td>
<td>20.8</td>
</tr>
<tr>
<td>Bag</td>
<td>4</td>
<td>7</td>
<td>15</td>
<td>10</td>
<td>9.9</td>
</tr>
</tbody>
</table>
The effect of two different resin sizes on size tests are compared in Table VI as obtained from hand sheets made from beater runs listed in Table III, page 47, and Table IV, page 49.
<table>
<thead>
<tr>
<th>Type of Plant</th>
<th>Surplus Yield (kg)</th>
<th>Surplus Yield (kg)</th>
<th>Surplus Yield (kg)</th>
<th>Surplus Yield (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Variety</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Dry Method</td>
<td>Wet Method</td>
<td>Dry Method</td>
<td>Wet Method</td>
</tr>
<tr>
<td></td>
<td>sec.</td>
<td>sec.</td>
<td>sec.</td>
<td>sec.</td>
</tr>
<tr>
<td>Alfalfa</td>
<td>20</td>
<td>25</td>
<td>22</td>
<td>28</td>
</tr>
<tr>
<td>Wheat</td>
<td>30</td>
<td>35</td>
<td>28</td>
<td>33</td>
</tr>
<tr>
<td>Soybean</td>
<td>15</td>
<td>20</td>
<td>16</td>
<td>21</td>
</tr>
<tr>
<td>Maize</td>
<td>25</td>
<td>30</td>
<td>24</td>
<td>29</td>
</tr>
<tr>
<td>Alfalfa</td>
<td>1.5</td>
<td>1.7</td>
<td>1.6</td>
<td>1.8</td>
</tr>
</tbody>
</table>

TABLE VI.
Figure No. III
The Relative Sizability of Pulps as Measured by Different Size Testing Methods

Temperature: 70°F
Relative Humidity: 65%
1. Valley Size Tester
2. Currier Size Tester
3. Dry Indicator
4. Corson Curl
5. DISCUSSION.

In the preceding sections of this investigation it was found that pulp fibers altered the system set up in the process of resin sizing. Instead of obtaining only the normal aluminum abietate as was found to be the case in the absence of fibers, free abietic acid as well as aluminum abietate was found in the resin precipitate. The relative amounts of free and combined resin varied with the individual pulp. It is a well known fact that in mill practice it is often more difficult to size certain types of pulps than others. In view of these two facts, beater runs were made on the same pulps that were used in Table II, pages 36, 37, 38, and 39 of this investigation, in order to determine whether any correlations existed between the relative amounts of free and combined resin present in the pulps and the relative ease of sizing of these pulp fibers.

a. Relative Sizability of Various Pulps.

In Tables III and IV, pages 47 and 49 respectively, are given the results obtained by making size tests on hand sheets made from beater runs on eight different pulps. The stocks were all beaten to approximately the same freeness and the hand sheets in all cases were made under exactly the same conditions. It can be seen that the relative degree of sizing of any one pulp as compared to another may vary depending upon the size test used; this is more or less an established fact in mill practice. In comparing the Valley size test of groundwood
with unbleached kraft, the groundwood test is higher while the reverse is true when the dry indicator test is used.

b. Effect of Free Resin on Size Tests of Various Pulps.

In Table V, page 51, is shown the size test data on beater runs from eight different pulps as compared to the amount of hydrolysis of the sodium abietate solutions in the presence of these pulps; the degree of hydrolysis being measured by the amount of free abietic acid found. The beater runs were carried out under identical conditions with those used in studying the equilibria of the sodium abietate solutions in the presence of pulp fibers. The same type of system was set up in all cases; namely, sodium abietate, aluminum sulfate, distilled water, and pulp fibers. There appears to be no definite correlation between any one size test and the extent to which the sodium abietate undergoes hydrolysis when the different pulps are compared with each other. No single size test employed gives results comparable with the relative quantities of free and combined resin present in the sheet.

c. Effect of Resins on Size Tests of Various Pulps.

Table VI, page 53, compares size tests on hand sheets made from beater runs of eight different pulps under standard conditions using two percent sodium abietate in one set and two percent commercial resin size (30% free) in the other. There appears to be no definite advantage in using a highly purified resin size such as sodium abietate. The commercial size, which is only partly saponified, gives no better
sate, then the fully saponified sodium abietate.

From the results obtained in Tables III, IV, V, and VI, pages 47, 49, 51, and 53 respectively, no definite advantages can be given to either free resin or aluminum resinate as the true sizing agent. However, this may be due to the failure of the size test employed to actually measure the true degree of sizing. Since a great many of the investigators in this field disagree as to the relative merits of free resin and aluminum resinate as sizing agents, it may be assumed that some of these disagreements are the result of different size testing methods being used by the various workers.

D. THE EFFECT OF DRYING TEMPERATURE AND ROUGH RETENTION ON THE SIZABILITY OF A GIVEN PULP.

1. METHOD OF PROCEDURE.

Hand sheets from beater rums, shown in Table III, page 47, were made under identical conditions; part of the sheets were dried at 105° C. for ten minutes and part were air dried. Sufficient air dried sheets were cut up into small pieces and extracted with chloroform in a Soxhlet extractor in order to determine the percentage of resin retained in the hand sheets. Samples of air dried and electrically dried sheets were seasoned in the humidity room at 70° F. and 65 percent relative humidity and then tested for their degree of sizing by means of different size tests.
2. DATA.

Hand sheets from better runs, in Table III, page 57, made under identical conditions, were air dried and dried at 105° C. for ten minutes. Samples of these sheets were tested for degree of sizing by four different size tests. The results are shown in Table VII.
<table>
<thead>
<tr>
<th>Type of pulp</th>
<th>Dried at 105° C.</th>
<th>Air dried</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Valley size test</td>
<td>Currier size test</td>
</tr>
<tr>
<td></td>
<td>sec.</td>
<td>sec.</td>
</tr>
<tr>
<td>Groundwood</td>
<td>42</td>
<td>102</td>
</tr>
<tr>
<td>Unbl. kraft</td>
<td>21</td>
<td>45</td>
</tr>
<tr>
<td>Unbl. Nitsch</td>
<td>14</td>
<td>26</td>
</tr>
<tr>
<td>Unbl. Sulfite</td>
<td>13</td>
<td>19</td>
</tr>
<tr>
<td>Semi N. Kraft</td>
<td>21</td>
<td>50</td>
</tr>
<tr>
<td>Blanché Sulfite</td>
<td>15</td>
<td>29</td>
</tr>
<tr>
<td>Alpha</td>
<td>18</td>
<td>31</td>
</tr>
<tr>
<td>Bag</td>
<td>4</td>
<td>7</td>
</tr>
</tbody>
</table>
Air dried sheets, from beater runs, in Table III, page 47, were extracted with chloroform to determine the percent resin retention of the various pulp fibers. Table VIII gives the retention figures for eight different pulps.
### TABLE VIII.

**EFFECT OF VARIOUS PULP FIBERS ON THE RETENTION OF ROSIN.**

<table>
<thead>
<tr>
<th>Type of pulp</th>
<th>Percent Resin added</th>
<th>Percent Resin found</th>
<th>Percent Resin blank</th>
<th>Percent Resin corr'd</th>
<th>Percent retention</th>
</tr>
</thead>
<tbody>
<tr>
<td>Groundwood</td>
<td>2.00</td>
<td>2.37</td>
<td>0.99</td>
<td>1.38</td>
<td>69.0</td>
</tr>
<tr>
<td>Uml. Kraft</td>
<td>2.00</td>
<td>1.77</td>
<td>0.69</td>
<td>1.15</td>
<td>59.0</td>
</tr>
<tr>
<td>Uml. Mitsch.</td>
<td>2.00</td>
<td>1.567</td>
<td>0.507</td>
<td>1.06</td>
<td>54.0</td>
</tr>
<tr>
<td>Uml. Sulfite</td>
<td>2.00</td>
<td>1.978</td>
<td>1.038</td>
<td>0.94</td>
<td>47.0</td>
</tr>
<tr>
<td>Semi. Bri. Kraft</td>
<td>2.00</td>
<td>1.399</td>
<td>0.039</td>
<td>1.38</td>
<td>66.0</td>
</tr>
<tr>
<td>Bleached Sulfite</td>
<td>2.00</td>
<td>1.735</td>
<td>0.756</td>
<td>0.96</td>
<td>48.0</td>
</tr>
<tr>
<td>Alpha</td>
<td>2.00</td>
<td>1.231</td>
<td>0.181</td>
<td>1.05</td>
<td>52.5</td>
</tr>
<tr>
<td>Rag</td>
<td>2.00</td>
<td>1.94</td>
<td>0.190</td>
<td>1.32</td>
<td>67.5</td>
</tr>
</tbody>
</table>
Table IX compares the resin retentions as obtained in Table VIII, page 61, with the four size tests as obtained in hester runs made in Table III, page 47.
<table>
<thead>
<tr>
<th>Type of Soil</th>
<th>Percent Reduction</th>
<th>Valley Slope Factor</th>
<th>Quarter Mile Factor</th>
<th>Canopy Cover Factor</th>
<th>Overall Loss Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ground Debt</td>
<td>69.0</td>
<td>0.8</td>
<td>0.7</td>
<td>0.8</td>
<td>1.3</td>
</tr>
<tr>
<td>Tobia. Match</td>
<td>59.0</td>
<td>0.8</td>
<td>0.7</td>
<td>0.8</td>
<td>1.3</td>
</tr>
<tr>
<td>Tobia. Sandite</td>
<td>37.0</td>
<td>0.8</td>
<td>0.7</td>
<td>0.8</td>
<td>1.3</td>
</tr>
<tr>
<td>Sand. Match</td>
<td>65.0</td>
<td>0.8</td>
<td>0.7</td>
<td>0.8</td>
<td>1.3</td>
</tr>
<tr>
<td>Sand. Sandite</td>
<td>30.0</td>
<td>0.8</td>
<td>0.7</td>
<td>0.8</td>
<td>1.3</td>
</tr>
<tr>
<td>Alpines</td>
<td>50.5</td>
<td>0.8</td>
<td>0.7</td>
<td>0.8</td>
<td>1.3</td>
</tr>
<tr>
<td>Meadow</td>
<td>67.5</td>
<td>0.8</td>
<td>0.7</td>
<td>0.8</td>
<td>1.3</td>
</tr>
<tr>
<td>Ridge</td>
<td>47.5</td>
<td>0.8</td>
<td>0.7</td>
<td>0.8</td>
<td>1.3</td>
</tr>
</tbody>
</table>
3. DISCUSSION


The fact that aluminum resinate is said to undergo decomposition by some investigators when dried at temperatures approximately that of the drier sections, and that this claim was confirmed in the present work, led to the following series of tests.

Sise tests are shown in Table VII, page 59, of hand sheets made from beater run of eight different stocks sized with two percent sodium abiate and sufficient alum to produce a pH of 4.5. The sise tests of air dried sheets and sheets dried at 105° C. for ten minutes are compared and in most cases the air dried sheets give better sise tests.

Since it was found that aluminum abiate partially decomposes at temperatures existing on the dryers and that aluminum resinate present in the sheet was decomposed at least in part in passing through the drier sections, the effect of this decomposition was investigated in relation to sizing results. This decomposition appears neither to help nor hinder the sise tests since sheets dried at 105° C. are in no way superior to air dried sheets in this respect. This would not seem to support the theory of some workers in this field that a continuous film is necessary for good sizing, and that this film is produced on the dryers.
Since no correlations were obtained between the composition of the resin precipitate and the relative ease of sizing of the various pulps as measured by four different size tests, the retention of resin by the various pulps was determined and compared with size tests of these pulps.

b. Effect of Various Pulp Fibers on the Retention of Resin.

Retention figures in Table VIII, page 61, obtained by extracting air dried sheets with chloroform show that in making hand sheets between forty-five and seventy percent of the resin is retained in the sheet when two percent sodium stearate and sufficient alum to produce a pH of 4.5 is used. The percent retention did not vary greatly between two extremely different paper fibers such as groundwood and rag.


A comparison of the different size tests and retentions by the various pulps as obtained in Table IX, page 63, shows that a higher resin retention by one pulp as compared with another does not necessarily mean a superior size test for that pulp. Although rag has a higher resin retention than some of the wood pulps, the size tests show a poorer sized sheet for rag. This also holds true when two different types of wood pulps are compared.

In mill practice intermittent sizing difficulties are often encountered, even though the same quality and quantity of size, stock, and other materials are the same. When the poorly sized sheets are
analyzed for resin, the retention is found to be just as good as the well sized sheets. This would indicate that particle size or distribution is an important factor in obtaining a well sized sheet.
CHAPTER V.

SUMMARY

The properties of the precipitate obtained on the addition of an excess of aluminum sulfate to a dilute sodium acetate solution have been investigated in order to develop an analytical method for studying the ionic mechanism.

It was found that the precipitate, when dried at 50° C. in a vacuum oven, was completely soluble in benzene, chloroform, and absolute ether but insoluble in absolute alcohol and acetone. When commercial ether containing small amounts of moisture was used, the precipitate went into solution; but on standing one hour, a resinous material settled out. Acetic acid is soluble in alcohol, benzene, ether, and chloroform.

The \( \text{Al}_2\text{O}_3 \) content of the precipitate was found to be in fair agreement with the \( \text{Al}_2\text{O}_3 \) content demanded by a neutral aluminum acetate, \( \text{Al}(\text{CH}_3\text{COO})_2 \), namely 5.50%.

The filtered moist aluminum acetate, when dried at 80° C. for ninety minutes, was decomposed into two portions; one of which was soluble in chloroform, benzene, and absolute ether, and a second
portion insoluble in those solvents. The soluble portion contained a low percentage of aluminum oxide, and probably consisted of a mixture of free abietic acid and aluminum abietate. The insoluble portion contained a high percentage of aluminum oxide and probably consisted of a mixture of two basic aluminum abietates. The same was found to hold true for a commercial paper. Air dried paper extracted with chloroform contained a higher percentage of resin and a higher $\text{Al}_2\text{O}_3$ content than the same paper that had passed through the drier sections. This substantiates the work of Hamilton, Kozlak, and Davidson (15) and Schute and Klimiszt (19); they studied the effect of heat on precipitates of aluminum abietate in the absence of pulp fibers.

In contrast to the optimism of Olsen and Gortnar (42), it was found that all of the resin precipitated on the fibers could be extracted with a neutral solvent such as chloroform if the sized fibers were air dried or dried in a vacuum oven at $50^\circ\text{C}$.

The reaction between an excess of aluminum sulfate on four different beater concentrations of sodium abietate was investigated in the absence of pulp fiber; only the normal aluminum abietate was formed by this reaction; the results obtained confirm the work of investigators such as Heuser (23), Olsen (39), and Schute and Klimiszt (19). However, when the same reaction was studied in the presence of eight different pulps at three different beater concentrations of sodium abietate, abietic acid as well as aluminum abietate
were precipitated on the fibers. The amount of free abietic acid was found to vary with different pulps and different concentrations of sodium abietate. The abietic acid present was due to the action of the pulp fibers in forcing the hydrolysis of the dilute sodium abietate solutions.

Soaker runs were made on the eight different pulps using both sodium abietate and commercial resin sizes containing thirty percent free resin.

In making size tests on hand sheets made from the various pulps it was found that the relative sizeability of the pulps varied depending on the size tests employed. This is also the case in mill practice.

Then the size tests were compared with the degree of hydrolysis of the sodium abietate solutions as affected by the various pulps; no definite relationship could be established. Size tests of hand sheets made from eight different pulps sized with sodium abietate are compared with size tests of sheets sized with a commercial resin size (30% free); no superiority of one resin over the other was apparent.

Size tests were made on air dried sheets as well as on sheets dried at 105° C. for ten minutes; in most cases the air dried sheets gave higher size tests. These results are in disagreement with
many investigators.

Air dried sheets were extracted with chloroform and their retentions determined; when the various pulps are studied there seems to be no apparent relationship between the size tests and the resin retentions. This is often found to be the case in mill practice.

Correlations between size tests and other variables studied were difficult due to variation in the relative solubility of the pulps when different size test methods were employed.

It must be assumed that the total quantity of resin present, including the various proportions of free resin and aluminum resinate, must be fundamentally related to the size characteristics of paper. Failure of any size test employed to reflect the factor in the finished sheet emphasises either the inadequacy of size tests now employed or perhaps the importance of certain mechanical and temperature effects which come into prominence with respect to sizing during the formation of the sheet.
CHAPTER VI.

CONCLUSIONS.

In this investigation it is concluded that:

1. Hand sheets that have been air dried or dried at a low temperature and paper that has not passed through the dryer sections can be extracted for its total resin content by means of a dry neutral solvent such as chloroform.

2. Drying temperatures as encountered by paper passing through the dryer sections are sufficient to decompose at least part of the aluminum resinate in the sheet. It is probable that part of the aluminum resinate is decomposed into basic aluminum resinates which are insoluble in chloroform making it necessary to use some other type of solvent for extraction.

3. It has been found that a precipitate of neutral aluminum abietate is formed from the interaction of an excess of aluminum sulfate with dilute sodium abietate. When pulp fibers are added to the system, however, the hydrolysis of a portion of the sodium abietate is forced as a result of the selective adsorption of alkali by the fibers, and free abietic acid is precipitated on the
fibers along with neutral aluminum abietate. Various pulps behave differently in the extent to which they force the hydrolysis of sodium abietate.

4. Pulps arranged according to their relative ease of sizeability as measured by one size testing method will fall in a different order when a different size testing method is used. Two different pulps may give entirely different relative degrees of sizing, depending on which size test was used.

5. The relative amounts of free resin and aluminum resinate formed in the sheet is controlled to a large extent by the character of the pulp and its action on sodium resinate; but none of the currently used tests for the degree of sizing give relative sizeabilities that are related with the quantity or relative amount of either free abietic acid or normal aluminum abietate.

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