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A Contribution to the Knowledge of Rosin Sizing

by H. W. Bialkowsky

June, 1933

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A Contribution to the Knowledge of Rosin Sizing

A Thesis submitted by

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H.V.B.

-Contents-

Introduction	Page 1
Historical Survey	3
Discussion-	
Statement of the Problem	9
The Hydrolysis of Sodium Resinate	10
Alkali Removal by Pulp Fibers	22
The Action of Pulp Fibers on Dilute Sodium Abietate Solutions	33
Experimental-	
Preparation of Abietic Acid	39
Preparation of Sodium Resinate Solutions	40
The Determination of the Hydrolysis of Dilute Sodium Abietate Solutions	40
The Conductivity of Dilute Sodium Resinate Solutions	53
Alkali Removal by Pulp Fibers	58
Effect of Temperature on Alkali Removal	62
Effect of Pulp Consistence on Alkali Removal	64
Behavior of Commercial Pulp Fibers toward Dilute Alkaline Solutions	65
Alkali Removal determined by Conductivity Methods	70
Effect of Pulp Fibers on the Hydroxyl Ion Concentration of Dilute Alkaline Solutions	73
The Effect of Pulp Fibers on Dilute Sodium Resinate Solutions	75
Summary	83
Conclusions	88

A Contribution To The Knowledge Of Rosin Sizing

*Introduction-

In the process of sizing paper with rosin, the rosin size, either as a neutral soap or as a free rosin size, is added to the slush fiber stock with the subsequent addition of alum. In some cases the alum is added to the pulp mixture before the addition of the rosin size. Such a system consisting of size, aluminum sulphate, cellulose fibers and water is an extremely complicated one, both physically and chemically. The colloidal properties and characteristics of cellulose alone present difficulties, but in the presence of colloidal electrolytes, such as alum and rosin size in dilute solution, the conditions become very complex. The concentrations of the rosin size and the alum in the beater are quite low, and the natural behavior of these constituents will probably be affected by the colloiddally active cellulose fibers. Under beater conditions, therefore, the action of the alum on the rosin size is probably not a simple chemical precipitation. Due to the hydrolytic effect of water and also the presence of the colloidally active cellulose fibers, the rosin size, initially added to the pulp mixture as a sodium soap, may possibly suffer a partial or complete chemical rearrangement with the formation of chemical aggregates other than the pure sodium soap. In order to understand the action of the alum on the rosin size in the pulp mixture, it is necessary to know the chemical and physical nature of the rosin size under these conditions just before the alum is

added. The present investigation was limited to a study of the nature of dilute sodium abietate solutions, and the action of various commercial pulp fibers on these solutions. The behavior of these pulp fibers toward dilute sodium hydroxide solutions was also investigated for the purpose of gaining a better understanding of the action of the pulp fibers on the resin soap solutions.

Historical Survey

In 1807, Moritz Illig, of Frankfort, Germany, devised a process for sizing paper with rosin soap while the stock was being prepared. Previous to that time, the comparatively small quantities of paper then produced were rendered water and ink resistant by surface sizing with starch or glue. Illig's process consisted of adding rosin soap to the stock in the hollander, with the subsequent addition of alum to coagulate the rosin. Illig's process is used throughout the paper industry today, with only very minor changes. The mechanism of the sizing process has been the subject of much discussion and experimental work. The literature on the subject is quite voluminous, and there are many differences of opinion. Only a brief review will be considered here, a more complete review can be found in the papers by Olsen and Gortner (*Paper Trade J.* 87:15,59-63,1928) and by Klein (*Zellstoff und Papier* 9:6,370-373,1929).

Illig's opinion of the mechanism of the process, was that the rosin was first rendered water soluble by saponification with alkali, and simply precipitated as free rosin in the stock mixture by the alum (*Papier-Zeitung* 12: Mrs. 34-41,1887. A reprint of Illig's original paper). Later, Orioli explained the mechanism of the sizing process on the assumption, that the precipitated aluminum resinate is the main agent responsible for the sizing action, and that the coagulated free rosin simply supports this action. In 1878, Wurster, probably unaware of the opinions of Illig, again propounded the theory, that free rosin is the main sizing agent (*Le Collage et la Nature du Papier*, 1878).

Cross and Bevan developed the theory that aluminum resinate is decomposed by the pulp fibers into free rosin and alumina, which are then adsorbed by the cellulose fibers and produce the sizing action.

Griffen has shown that neither free rosin or aluminum resinate alone can produce efficient sizing, and that both are necessary (J.A.C.S. 27:258-263, 1905).

During the past thirty years, many investigators have presented experimental data and opinions concerning the mechanism of the rosin sizing process, but with many conflicting results. Several authors maintain that free rosin is the main sizing agent, while others believe to have evidence in favor of aluminum resinate as the principal agent. Included are Arledter, (Papier Ztg. 32; 773-774, 1907); Remington, Bowach and Davidson, (Ind. Eng. Chem. 3; 466-471, 1911); Neugebauer, (Z. angew. Chem. 25; 2155-2159, 1912); Sieber, (Paper Trade J. 75; Wrs. 15-17, 1922); Stoeckigt and Klinger, (Papierfabr. 19; Fest und Auslands Heft 50-60, 1921); Heuser, (Svensk Pappertid. 26; 114-115, 202-205, 1923); Beltzer, (Industrie Chimique 1924, 56-61, 147-149) and many others.

Zherebov (Bumazhnaisa Promyshlenost II; 1, 59-77; 4, 391-414, 1923) disagrees with the colloidal theory of Sieber, Lorenz, and Stoeckigt and Klinger. According to Zherebov, the active sizing acids of colophony are crystalloidal although the sizing solution is colloidal. If the union of aluminum hydroxide and rosin is merely the adsorption of one colloid on another, then amount of aluminum hydroxide in the combination should vary. But he states that the results of Remington et al, Heuser and Sieber

show nearly the same amount of aluminum oxide, namely 4.78-5.69 percent. Making allowance for variation in the acid number of different rosins, Zharebov concludes that the alum and rosin enter into chemical reaction. Also according to Zharebov, only those compounds have a sizing action which are chemically active, that is, those that are unsaturated and have double bonds.

Klemm (Wochbl. Papierfabr. 39; 1369-1372, 1908) has pointed out the great importance of physical conditions, such as the manner of beating, the influence of drying, etc. The preparation of the stock, the thermal conditions in the beater, jordan and chests, as well as the handling of the stock on the machine and through the dryers have been found to be of fundamental significance in obtaining the desired sizing results.

Ostwald and Lorenz (Kolloid Z. 32; 119-137, 195-209, 1923) (Colloid Chemistry, Alexander, Vol. IV, Chapter III) come to the conclusion that aluminum sulphate and sodium resinate are hydrolyzed in the beater. Cellulose fibers are electronegative, alum treated fibers are positive, and colloidal rosin is negatively charged. The positively charged alumina is adsorbed by the fibrous interfaces of the negatively charged cellulose fibers. Alumina also forms a positive layer around the electronegative rosin particles, so that the colloidal alumina acts as an electrostatic binding material between the fibers and the rosin. Lorenz also found that aqueous solutions of sodium resinate are on the boundary line between molecular dispersoids and typical colloids and that free rosin is a typical colloidal suspension with a negative charge.

Thiriet and Delcroix, the discoverers of the Delthirna process for the preparation of rosin size, were probably the first investigators to determine the effect of hydrogen ion concentration on rosin sizing (Paper 35; 2, 51-55, 1924). They obtained the best sizing at pH 4.5-5.0. They consider that at pH 4.5-5.0, the cellulose and the rosin have opposite electrical charges, and that the sizing is produced by a union between the rosin with a positive charge and the electronegative cellulose fibers. Above and below this range of hydrogen ion concentration, the rosin and the cellulose have electrical charges of the same sign and the sizing remains incomplete.

Shaw (Paper Trade J. 81; 10, 59-62, 1925) was able to show by practical experiments that at pH 5.0-5.5, the conditions are the most suitable for the attainment of complete sizing, with a possible saving of 33 percent on alum.

According to Roschier (Pappers Trävaru-tid. Finland 1927) at a pH 3.7-3.9, only a small amount of aluminum resinate is formed which is held directly by the fibers, and under these conditions alumina is also chemically bound by the fibers, which together with the resinate give the fibers a positive charge, so that the negatively charged free rosin can unite with the fibers. A large portion of the alum is lost under these conditions. At pH 4.5-5.0, sodium resinate is transformed mainly into the aluminum salt, which is directly bound by the fibers. Excess alum forms the electropositive colloidal hydrate of alumina, which combines with the colloidal free rosin to form electropositive adsorption compounds. These adsorption compounds can then be taken up by the negatively charged cellulose fibers.

The effect of heating the moist paper on the final sizing has been investigated by Oeman (Pulp Paper Mag. Can. 26; 1651-1656, 1928) Oeman found that strong heating of the moist paper sheet is detrimental to the sizing, and that the injurious effects are at a minimum at a hydrogen ion concentration of pH 4.0-5.0.

Olsen and Gortner (Paper Trade J. 37; 16, 47-50, 1928) found that the adsorption of rosin by fibers is a function of the time, so that the process must be a colloidal phenomenon rather than a purely chemical reaction. The adsorption of the rosin depends upon the ash content of the fibers, and the most suitable hydrogen ion concentration for efficient sizing also depends on the ash content of the fibers. For various pulps, the most favorable pH value falls between 4.5 and 6.5.

Kanamaru (J. Soc. Chem. Ind. Japan 34; 242-252, 1921) has made a detailed study of the effect of zeta potential of the cellulose fibers on the sizing process. His results indicate that the sizing efficacy depends upon the quality and nature of the pulp, and that a decidedly negative pulp has, in general, a better sizing efficacy.

The degree of dissociation of rosin size has been investigated by Haug (Paper Trade J. 76; 26, 45-48; 77; 2, 51-54, 1923). According to Haug, sodium resinate when highly diluted with distilled water, undergoes hydrolysis which is approximately 100 percent. These results are based on measurements of the electrical conductivity of sodium resinate solutions and on purely chemical tests.

According to Ivanoff (Bumashnaia Promyshlennost I; 33, 1922) at a dilution of 0.5 gram per liter of rosin, as much as 95 percent of the rosin is free. Ivanoff concludes that at the dilution of the

beater, practically all of the rosin is hydrolyzed and in the free condition.

Beedle and Bolam (J. Soc. Chem. Ind. 40; 4, 27T, 1921) following the work of McBain on the constitution of soap solutions, have determined the extent of hydrolysis of several commercial soaps at 90 deg. C. For sodium abietate solutions, they found the extent of the hydrolysis of 0.024 and 0.012 normal solutions to be 4.0 and 5.7 per cent respectively.

The preceding remarks are but a brief summary of the literature on rosin sizing. There are a great many papers dealing with all phases of the subject, and a review of all of them cannot be given here. There is a great deal of confusion and controversy in the work reported, but this is undoubtedly due to the difficulty of controlling the conditions of the experiments.

-DISCUSSION-

Statement of the Problem:-

The present study is concerned only with the nature of dilute sodium resinate solutions and the effect of various commercial pulps on these solutions. It is necessary to know the extent of the hydrolysis of sodium resinate solutions at beater concentrations, and the effect of pulp fibers on the hydrolysis of the soap, in order to understand the action of subsequent additions of alum. The literature on the hydrolysis of rosin sizing solutions at beater concentrations contains various conflicting reports. In some cases, complete hydrolysis is assumed, without any concrete experimental data, in other cases, the extent of the hydrolysis is reported with very little information concerning the methods of measurement. This study may be divided into the following three main parts:

- 1). The determination of the extent of the hydrolysis of sodium resinate solutions at beater concentrations.
- 2). The effect of various commercial pulps on dilute sodium hydroxide solutions.
- 3). The effect of various commercial pulps on dilute sodium abietate solutions.

The concentration of the size in the beater will vary with the furnish of the rosin, and the consistency of the stock in the beater. The consistency of the stock in the beater is generally 3 to 6 percent. The furnish of the rosin size will vary from 1/2 to 5 percent or higher, depending on the paper being produced.

The following table shows the normality of the size in the beater, assuming the size to be neutral sodium resinate, at various consistencies of stock, and for various size furnishes based on the stock:

Consistency of Stock-----1%	Normality of Sodium Resinate				
	1	2	3	4	5
1	.0003	.0006	.0009	.0012	.0015
2	.0006	.0012	.0019	.0025	.0031
3	.0009	.0019	.0028	.0037	.0046
4	.0012	.0025	.0037	.0049	.0062
5	.0015	.0031	.0046	.0062	.0077
6	.0019	.0037	.0055	.0074	.0093

The concentration of the size in the beater, under most operating conditions, will fall in the range between N/2000 and N/100.

In these experiments it was advisable to work with a rather pure form of rosin, and throughout this entire study, the sizing solutions were prepared from pure abietic acid. The abietic acid was prepared according to the method reported by Steele (J.A.C.S. 44; 1333, 1922). An outline of this method is given below.

The Hydrolysis of Sodium Resinate

The system consisting of size, aluminum sulphate, cellulose fibers, and water, is an extremely complicated one, both physically and chemically. The colloidal characteristics and properties of cellulose alone present difficulties, but in the presence of colloidal electrolytes, such as alum and rosin size in dilute solution, the conditions become very complex. The concentrations of the rosin size and the alum in the beater are quite low, and

the natural behavior of these constituents will probably be affected by the presence of the colloiddally active cellulose fibers. In more concentrated solutions in the absence of pulp fibers, sodium resinate and aluminum sulphate could react with one another with the formation of aluminum resinate. But in the concentrations prevailing in the beater, $\text{N}/1000$ to $\text{N}/100$, the chemical stability of both the alum and the soap are not very great, and the stability of these constituents could readily be affected by the presence of the pulp fibers. Sodium resinate is a salt of a strong base and a very weak acid and in very dilute solutions, hydrolysis takes place with the formation of colloidal rosin; due to the extremely low solubility of abietic acid in water, only a very small fraction of the abietic acid is in true molecular solution. Aluminum sulphate is a salt of a very strong acid and a weak base, and at lower concentrations, hydrolysis takes place with the formation of colloidal alumina. In these dilute solutions, the aluminum is partly present as ionic aluminum and partly as a colloidal dispersion of alumina. When dilute sodium resinate solutions are allowed to react with dilute aluminum sulphate solutions, there are probably several products formed by the reaction. The rosin present as the sodium soap could be precipitated by the aluminum ions or by the acidity of the resulting solution as aluminum resinate and free abietic acid respectively. The colloidal free rosin originally present, and that formed by the reduction in the original alkalinity by the acid of the alum, could form adsorption products with the colloidal alumina. It is quite difficult to distinguish between the true

aluminum resinate that may be formed, and the rosin-alumina adsorption products. The aluminum resinate, it is true, should have a very definite chemical composition, as compared to the variable composition of the adsorption compounds. But under the conditions of these precipitations, the aluminum resinate precipitate could form adsorption compounds with any colloidal materials present, so that the resulting precipitate will have a more or less indefinite composition. If only colloidal adsorption compounds are formed, the average chemical composition of the precipitate cannot vary very much from the chemical composition of true aluminum resinate, since chemical equivalent quantities of the reactants are very nearly consumed in the precipitation regardless of the nature of the final product.

The characteristics and properties of soap solutions have been carefully studied by McBain and his collaborators (J. Soc. Chem. Ind. 37; 249T, 1918). After considerable experimental work, requiring very painstaking measurements, McBain developed a comprehensive theory of soap solutions, which he defines as colloidal electrolytes. This theory is based on the hypotheses that all these solutions are salts in which one ion is replaced by an ionic micelle, which exhibits high conductivity and great solvation, and which carries a great number of electrical charges. The concentration of the solutions is a very important factor, in very dilute solutions the soap exhibits the properties of a simple electrolyte, while concentrated solutions and the addition of other substances may lead to the formation of a neutral colloid. The conception of an ionic micelle of great valency and

hydration explains the really high conductivity and also the high mechanical viscosity. His work also establishes the important theoretical results that colloids and colloidal electrolytes may participate in true, perfectly reversible and reproducible equilibria.

According to McBain, in the case of very dilute solutions, the soaps are partially hydrolyzed according to the following equation:-



The acid is considered to be in suspension, either coarse or colloidal as the case may be, and to consist of something between the neutral salt NaR and the acid soap NaHR_2 , where R is the radical of the fatty acid. Free fatty acid can only exist in excessively small amounts in such soap solutions, even in the presence of a large excess of free fatty acid. The above equations differs from the usually accepted course of hydrolysis which is generally expressed as follows:-



The free acid in this case either remains in a colloidal suspension or is precipitated. The data which establish the conception of an acid soap are based upon direct analysis, conductivity measurements, measurements of electromotive force, and measurements of the free hydroxyl ion by the rate of catalysis of nitrosotriacetone.

In dilute solutions, decinormal or somewhat less, soaps are composed of simple electrolytes in true solution, with simple ions. In decinormal solution, hydrolysis is still present, but

only in a very minor degree, since the hydroxyl ion concentration was shown to be only about $N/1000$. With increasing concentration, the fatty acid ions rapidly coalesce to form the ionic micelles described above, until in $N/2$ or $N/1$ solution the colloidal electrolyte comprises all the soap, hydrolysis being still more insignificant. With further increase in concentration the ionic micelle becomes less solvated and conducts even better, the only crystalloidal constituent left is the metallic ion, for the undissociated soap is now also in the colloidal form.

Prior to the work of McBain, much diversity of opinion existed as to the degree of hydrolysis of soap solutions, due mainly to the employment of unsuitable methods, such as direct titration, which disturbs the equilibrium and is bound to lead to erroneous results. The quantitative data of McBain show that all soap solutions are alkaline varying from $N/30000$ to $N/300$ for pure soap solutions, down to $N/30000$ for acid sodium palmitate, $NaHP2$. Several percent excess of alkali is required to drive back the hydrolysis completely, but not more than a few percent of this alkali can be sorbed by the soap even in the presence of a large excess of alkali, which means that the hydrolysis must be equal to the alkalinity.

Soaps exhibit a rather high proper conductivity, and in concentrated solutions the conductivity is abnormally high (Banbury and Martin, Chem.Soc.Trans. 1914, 105, 417). In the case of the higher soaps, the electrical conductivity, after passing through a minimum at about $N/10$, rises with increase in concentration up to nearly normal solution. This further

substantiates the hypothesis of an ionic micelle of conductivity intermediate between that of sodium and potassium ions, which was deduced from other considerations. The formation of the more highly conduction micelle from the comparatively a slow, large true ion, and the change of the micelle-ion equilibria with change in concentration are mirrored in the conductivity curves.

In soap solutions which are clear and approximately homogeneous, a low temperature favors the formation of colloidal micelle, and this micelle is more hydrated than at higher temperatures. The adjustments in the equilibria of the solution due to changes in temperature are made very quickly, and are very soon complete to within one percent, which makes it possible to readily obtain reproducible conditions.

In studying the hydrolysis of these soap solutions, McBain found the method of measuring hydroxyl ion concentration by the catalytic decomposition of nitrosotriacetoneamine quite useful in checking the results of other methods of measuring this hydrolysis due to the nature of these solutions, especially at higher concentrations, it was necessary to work at higher temperatures to obtain more or less homogeneous solutions over a wide range of concentration. For this reason most of the measurements on the hydrolysis of soap solutions were carried out at about 90 deg.

C. Some experimental difficulties arise in making electromotive force measurements under these conditions, but McBain succeeded in obtaining good agreement between the electromotive force method of measuring the hydrolysis and the method depending on the rate of the catalytic decomposition of nitrosotriacetoneamine. This

method was developed by Francis and his collaborators (J. Soc. Chem. Ind. 37:14, 252T, 1918), and has also been studied and used by a number of other investigators.

The hydrolysis of soap solutions, measured by the rate of catalysis of nitrosotriacetoneamine was investigated by McBain and Bolam (Chem. Soc. Trans. 1918, 113, 825). The method of measurement was based on that of Francis, involving the measurement of the volume of the nitrogen gas liberated. The authors found these results in good agreement with the hydrolysis values obtained by electromotive force determinations. Beedle and Bolam (J. Soc. Chem. Ind. 40: 4, 27T, 1921), determined the hydrolytic alkalinity of pure and commercial soaps, using the same method. The following table reported by these authors shows the extent of hydrolysis of several commercial soaps at 90 deg. C.:

Soap	Concentration of Soap	Concentration of Hydroxyl ion	Percent Hydrolysis
Sodium Oleate	.1 N-2.7%	.00079 N	.81
Sodium Oleate	.05 N-1.4%	.00098 N	1.99
Sodium Oleate	.02 N-.6%	.00074 N	3.7
Sodium Oleate	.01 N-.3%	.00066 N	6.6
Sodium Oleate	.002 N-.06%	.00055 N	28.1
Sodium Abietate	.024 N-1.0%	.00098 N	4.0
Sodium Abietate	.012 N-.5%	.00069 N	5.7

The above table shows that for an N/100 sodium resin solution, the degree of hydrolysis is about 6 percent at 90 deg. C. The degree of hydrolysis would be much lower than this value at room temperature. In a beater with the stock at a consistency of six percent, and a size furnish of six percent, the concentration of the size in the beater water would amount to approximately

N/100, assuming the size to be neutral sodium resinate. If we neglect for the present, the effect of impurities in the water, and the influence of the presence of the stock on this dilute soap solution, we could expect in a beater of stock under these conditions, that the size is still present as sodium resinate at least to the extent of ninety five percent.

The degree of dissociation of rosin size has been investigated by Haug (Paper Trade J. 76: 26, 45-48; 77:2, 51-54, 1923). According to Haug, sodium resinate, when highly diluted with distilled water, undergoes hydrolysis which is approximately 100 percent. These results are based on electrical conductivity measurements of sodium resinate solutions and on purely chemical tests.

According to the cryoscopic measurements of Ivanoff on sodium resinate solutions (Bunashnaia Promyshlenost I: 33, 1022) at a dilution of 0.5 gram of rosin per liter, as much 95 percent of the rosin is free. Ivanoff concludes that at the dilution of the beater, practically all of the rosin is hydrolyzed and in the free condition.

In view of the contradictory results on the degree of hydrolysis of sodium resinate reported by Beedle and Bolam on the one hand, and by Haug and Ivanoff on the other, the author investigated the extent of the hydrolysis of these dilute solutions. The hydrolysis values were determined by measuring the hydroxyl ion concentration by a method based on the catalytic decomposition of nitrosotriacetoneamine. Measurements were also made on the electrical conductivity of sodium resinate solutions for the purpose of noting any changes in the nature of the soap solutions

with dilution. These measurements are described in detail in the Experimental Part given later.

Employing a method based on the catalytic decomposition of nitrosotriacetoneamine by hydroxyl ions, the author found the extent of the hydrolysis of an N/100 sodium abietate solution at 30 deg. C. to be 0.50 percent. For an N/300 sodium abietate solution at 56 deg. C., the extent of the hydrolysis was found to be 4.3 percent. These values appear to be in good agreement with the values obtained by Beedle and Bolam. For 0.024 N and 0.012 N sodium abietate solutions at 90 deg. C. these investigators found the extent of the hydrolysis to be 4.0 and 5.7 percent respectively. At lower temperature, the hydrolysis of these solutions will undoubtedly be somewhat lower. Hydrolysis measurements involving the direct determination of the hydroxyl ion concentrations seem to indicate that at beater concentration under normal temperature conditions, the neutral rosin soap is not appreciably affected by the hydrolytic effect of water.

Any great changes in the nature of soap solutions upon dilution, due to the hydrolytic effect of water, should be reflected in the electrical conductivity curves of the solutions. The conductivity values of soap solutions are relatively high when compared with other salts of large molecular size but they are much lower than the values for sodium hydroxide solutions of the same molar concentration. If we assume that the hydrolysis of the soap results in the formation of free colloidal abietic acid and free sodium hydroxide, as given in the following equation:



then at infinite dilution hydrolysis should be complete, and the equivalent conductance of the soap solution should approach the equivalent conductance of sodium hydroxide, since on complete hydrolysis one equivalent quantity of free alkali is liberated.

The following tables show the results obtained for the specific and equivalent conductances of sodium resinate solutions at 25 deg. C. The corresponding values for sodium hydroxide solutions at the same temperature are also given for comparison.

Sodium Abietate Solutions

Concentration	Specific Conductance	Equivalent Conductance
.002 N	.000153	76.5
.004	.000296	74.2
.006	.000437	73.2
.008	.000565	70.6
.010	.000685	68.5
.0557	.00282	50.7
.1113	.00508	45.7

Sodium Hydroxide Solutions

Concentration	Specific Conductance	Equivalent Conductance
.00135	.000330	245
.00364	.000895	245
.00548	.00135	245
.00756	.00184	244
.00944	.00228	242

These values are shown graphically in Figures 1 and 2. In Figure 1 the specific conductances are plotted against the concentration, and Figure 2 shows the trend of the equivalent conductance with concentration. The specific conductance is very nearly directly proportional to the concentration for both the hydroxide and the resinate throughout the concentration range under consideration.

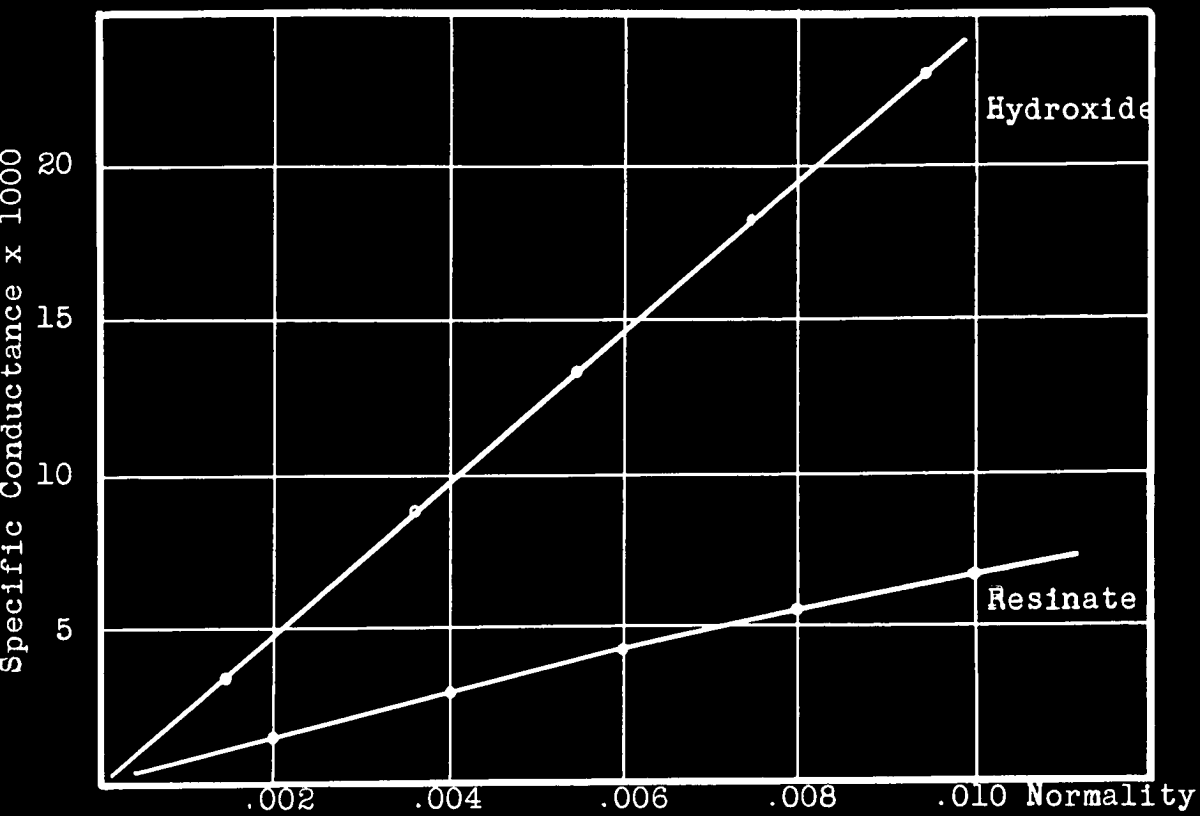


Fig.1. Specific Conductance of Sodium Hydroxide and Resinate Solutions

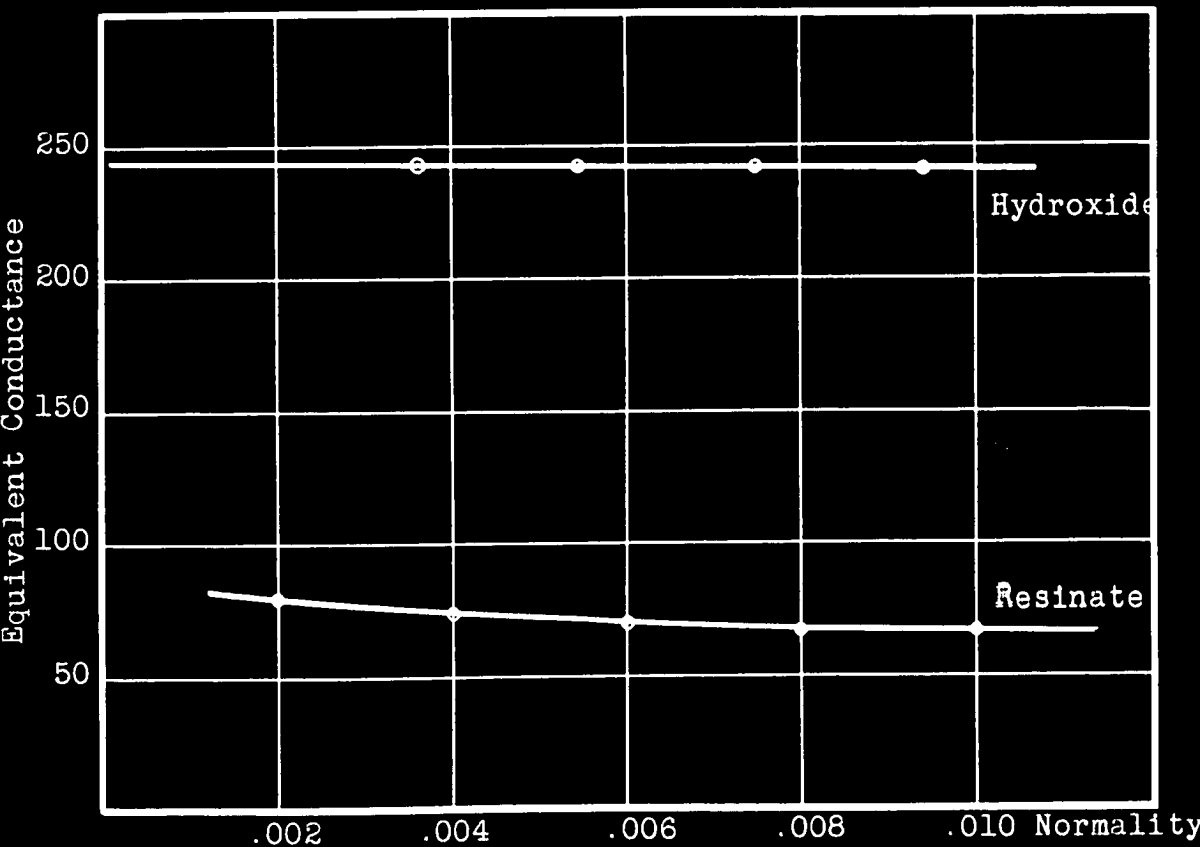


Fig 2. Equivalent Conductance of Sodium Hydroxide and Resinate Solutions

The equivalent conductance curve of the hydroxide is practically a straight line and very nearly horizontal. The equivalent conductance of the resinate rises gradually with increase in dilution. This increase may be due to the greater activity of the ions with dilution, and also the hydrolytic breakdown of the resinate into free hydroxide and colloidal abietic acid. The slope of this curve becomes greater with increase in dilution, but even at the concentration of $N/500$, the slope is not very great and the equivalent conductance of the soap is still far below that of the hydroxide. The results seem to indicate that the hydrolytic effects are becoming greater with increase in dilution, but throughout the concentration range under consideration, the hydrolysis of the soap is not very great, and that a large percentage of the rosin is still present as the sodium salt.

The conductivity measurements, therefore, are in good agreement with the results obtained on the hydrolysis of rosin soap by the method involving the determination of the hydroxyl ion concentration. At better concentrations, the pure neutral rosin soap is hydrolyzed only to a very slight extent, and the major portion of the rosin is still present as the sodium salt. These results are in good agreement with the work of Beedle and Bolan, and contrary to the work reported by Haug and by Ivenoff.

The previous discussion was limited to the behavior of pure dilute sodium resinate solutions. The hydrolysis equilibrium is partially determined by the concentration of the small amount of free alkali formed by the hydrolysis. Any condition which will affect the concentration of this free alkali will also affect the

hydrolysis equilibrium of the soap. A decrease in the free alkali concentration will favor a further hydrolysis of the soap to re-establish the equilibrium conditions. Under beater conditions we are dealing with a relatively large cellulose-water interface, and the fiber surfaces are capable of removing ions from the solution by colloidal forces. In the following pages, the action of various types of commercial pulp fibers on dilute sodium hydroxide solutions will be discussed. A knowledge of the effect of the pulp fibers on solutions of low alkali concentrations should be of value in determining the effect of the pulp fibers on the hydrolysis equilibrium of the rosin soap.

Alkali Removal by Pulp

The action of alkalis on cellulose has been a subject of great importance in the field of cellulose chemistry. The majority of the work reported in the literature, however, is concerned with the behavior of cellulose toward strong caustic solutions. It is known that even in very dilute alkali solutions the presence of cellulosic material has a tendency to lower the alkalinity of the solutions.

Figure 3 shows the effect of pulp fibers on the alkalinity of sodium hydroxide solutions over the concentration range from N/500 to N/100 sodium hydroxide. The loss in alkalinity will vary with the initial concentration of alkali, the consistency and nature of the pulp, the time of contact of the fibers with the solution and the temperature. The experimental methods employed in obtaining these curves are given in detail in the experimental part of this paper. In Figure 3, the percent of the available

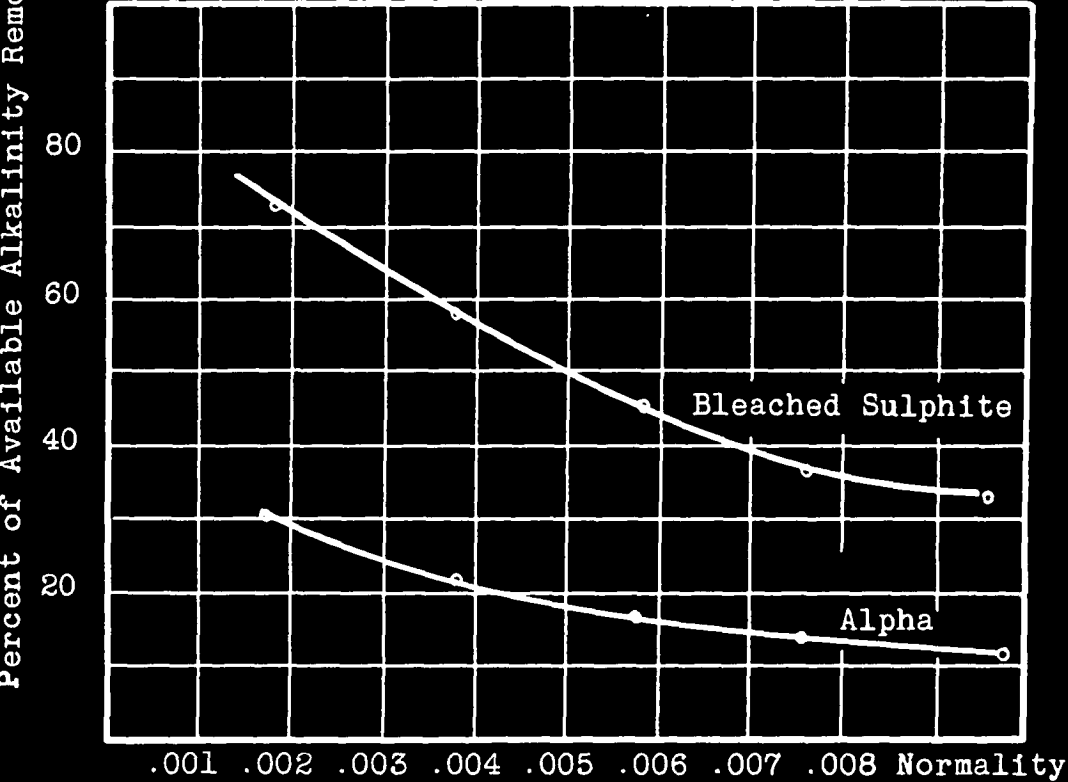
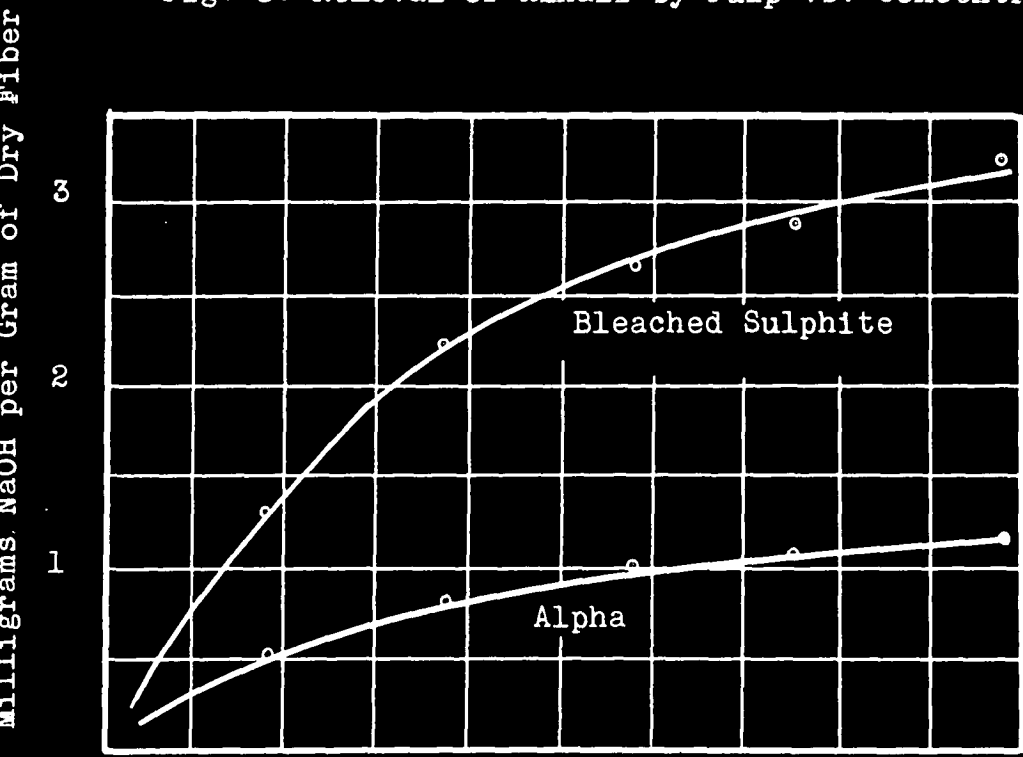


Fig. 3. Removal of Alkali by Pulp vs. Concentration



alkalinity removed by the fibers is plotted against the initial alkali concentrations, for two different types of pulp. The Bleached Sulphite fibers lower the alkalinity of the solutions to a much greater extent than the Alpha fibers. At the lower concentrations, the former removes almost 80 percent of the available alkalinity, whereas the latter removes about 30 percent. In Figure 4, the milligrams of sodium hydroxide removed from solution per gram of dry fiber are plotted against the original alkali concentrations. These curves resemble typical adsorption isotherms, but further evidence seems to indicate that the loss in alkalinity is not strictly an adsorption process.

The effect of the time of contact of the cellulose fibers with the solution on the loss in alkalinity is shown in Figure 5. The percent of the available alkalinity removed is plotted against the time of contact of the fibers with the solution, at three different initial alkali concentrations. The loss in alkalinity increases with the time of contact, and even after eighty hours of contact, absolute equilibrium conditions are not attained. Equilibrium conditions are more nearly attained for the more concentrated solutions than for the very dilute solutions.

If the removal of the alkalinity were due to pure adsorptive processes, then lower temperatures would favor greater adsorption. The effect of temperature on the loss in alkalinity is shown in Figure 6. In this figure the percent of available alkalinity removed is plotted against the time of contact of the fibers with the solution, at two different temperatures, all other conditions remaining constant. A larger percentage of the available alkalinity

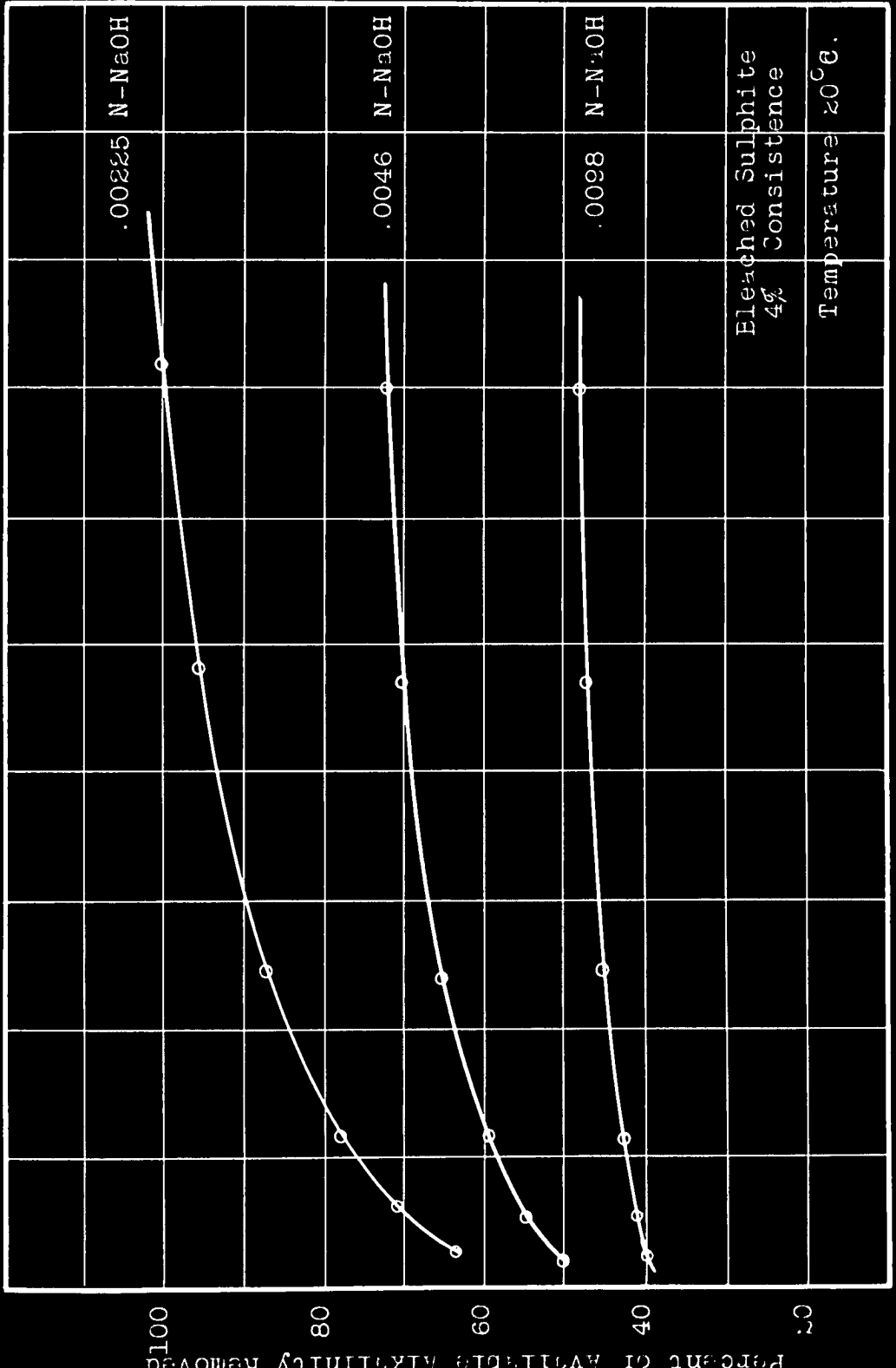


Fig. 5. Removal of Alkali by Pulp from Dilute NaOH Solutions with Time

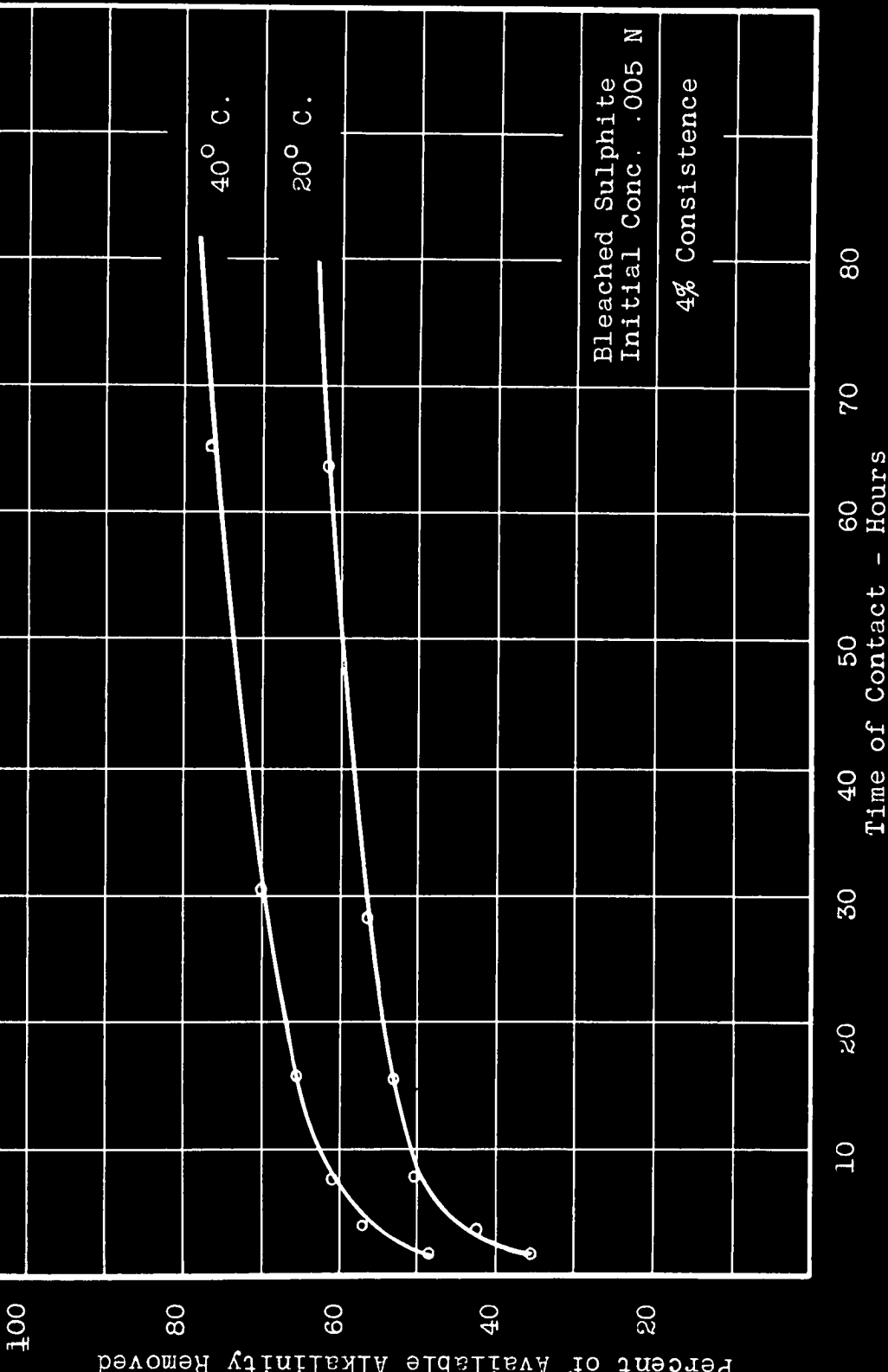


Fig. 6. Alkali Removal by Pulp with Time at 20° and 40° C.

is removed at 40 deg. C. than at 20 deg. C. These results indicate that the alkali removal is not strictly a process of adsorption, but probably a combination of adsorption, absorption and neutralization. In this connection, however, our main concern is the fact that the alkalinity is reduced regardless of the actual mechanism of the removal.

Figure 7 shows the effect of change in pulp consistence on the loss in alkalinity of the solution. The solid curve gives the percent loss in alkalinity plotted against the pulp consistence and the broken curve shows the milligrams of sodium hydroxide removed per gram of pulp plotted against consistence.

The previous discussion shows the effect of several factors on the removal of alkalinity by pulp fibers. In Figures 3 and 4, the difference in activity of two distinct types of pulp fibers toward alkali removal is illustrated. The loss in alkalinity appears to be determined, to a very great extent, by the nature of the pulp fibers. The differences between various types of commercial pulp fibers with regard to their activity toward lowering the alkalinity of sodium hydroxide solutions was investigated. Figure 8 and 9 show the effect of several pulps on dilute sodium hydroxide solutions. In Figure 8, the percent available alkalinity removed is plotted against the original alkali concentrations, and in Figure 9, the milligrams of sodium hydroxide per gram of pulp is plotted against the original alkali concentration. In every case, the percent of the available alkalinity removed increases with increases in dilution. These data also seem to indicate that the percent alkalinity removal approaches 100 percent

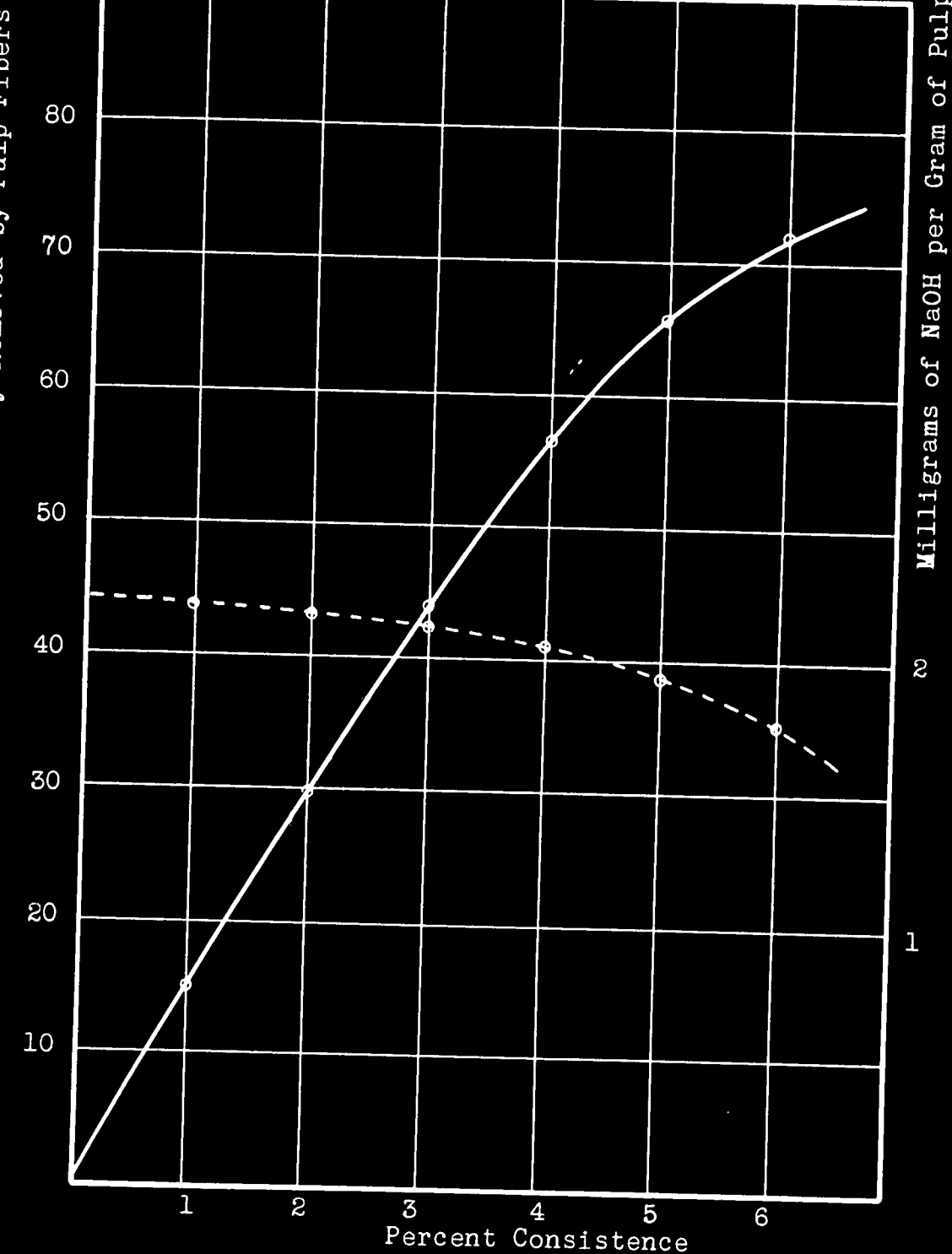


Fig. 7. Removal of Alkali with Change in Pulp Consistency

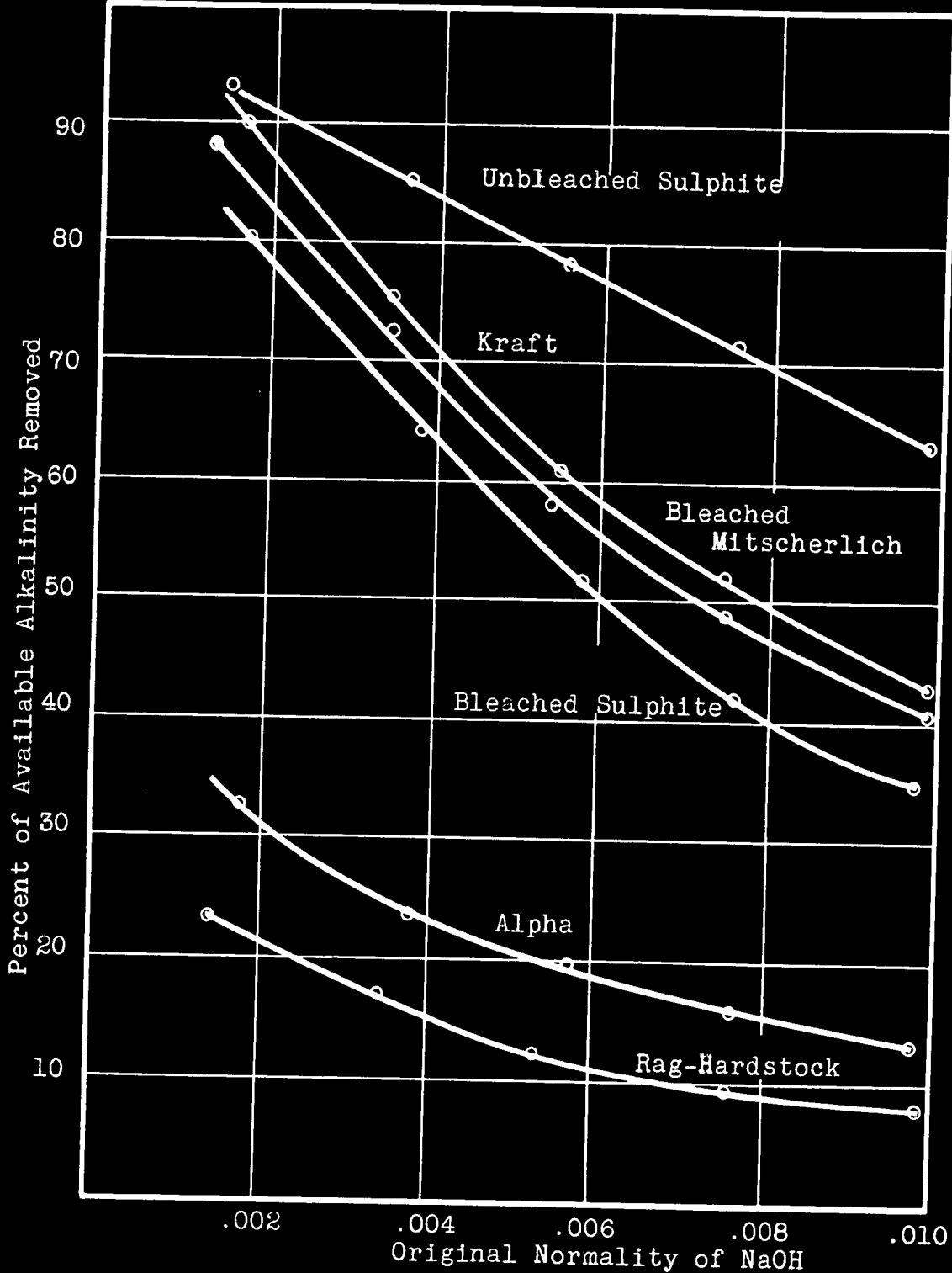


Fig.8. Alkali Removal from Dilute Sodium Hydroxide Solutions by Commercial Pulps

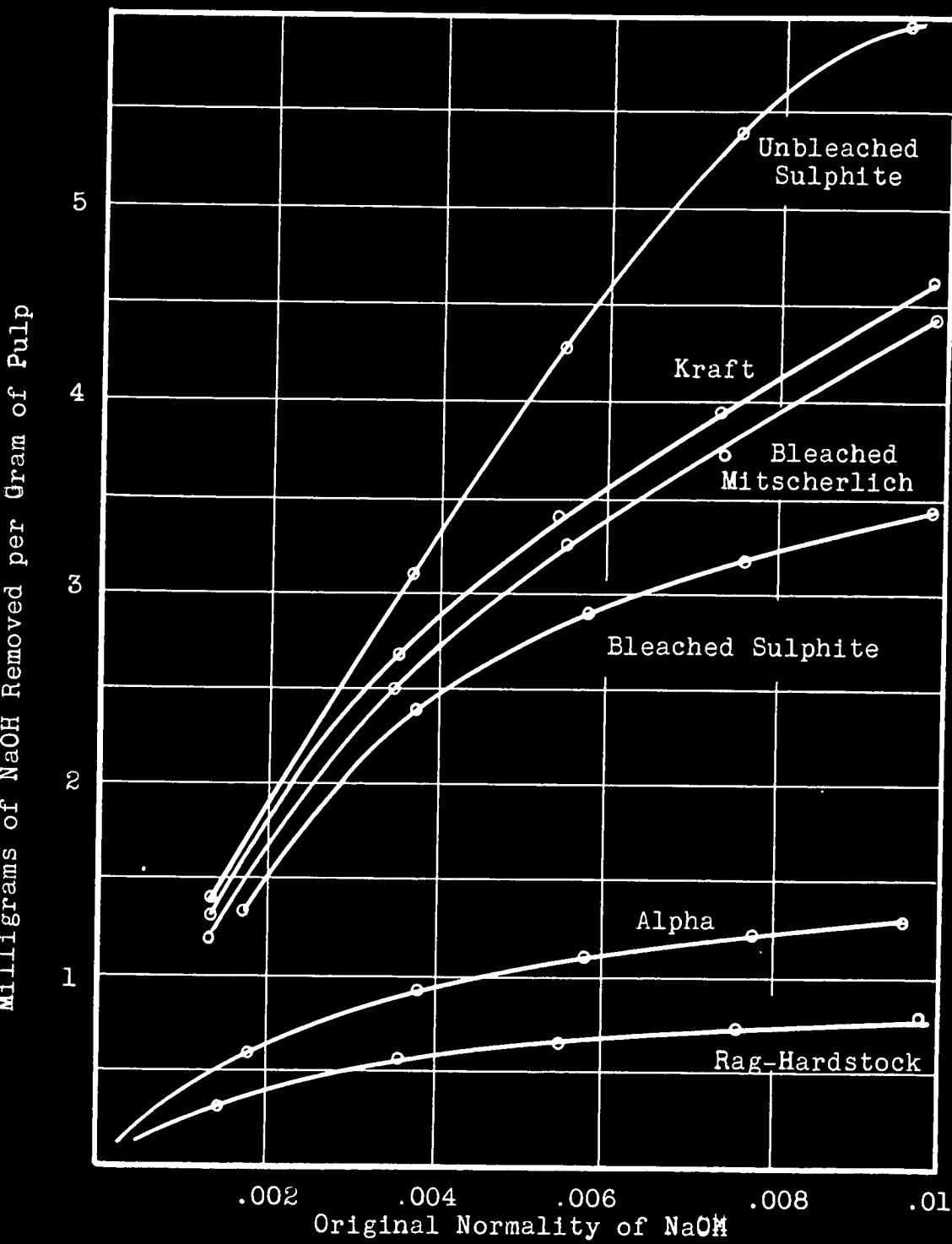


Fig.9. Alkali Removal from Dilute Sodium Hydroxide Solutions by Commercial Pulps

at infinite dilution. The kraft and sulphite pulps remove over 80 percent of the available alkalinity at the initial concentration of N/500. The particular sample of unbleached sulphite used in this case was from a rather raw cook. This pulp shows a pronounced tendency to lower the alkalinity over the entire concentration range. The sulphite pulp, bleached Mitscherlich sulphite, and the ordinary bleached sulphite samples follow the unbleached sulphite in the decreasing order of their activity toward dilute alkali solutions. The Alpha fiber exhibits a much lower activity than the other wood fibers and finally the rag-hardstock (Muslins) shows only a slight tendency toward alkali removal. These results indicate the great difference in the activity of various commercial pulp fibers on dilute alkaline solutions. It is interesting to compare the order of the activities of the various pulps. In general, the purer the pulp the more difficult it is to obtain good sizing in the resulting sheet. Rag-stock is more difficult to size than the size than the ordinary wood pulps. It is also interesting to compare the action of this series of pulps on sodium hydroxide solutions with the results obtained on the action of the same on dilute sodium abietate solutions. As will be shown later, the action of the various pulps toward sodium hydroxide solutions is quite analogous to the behavior of these pulps toward the sodium abietate solutions.

All of the measurements just described on the lowering of the alkalinity of dilute sodium hydroxide solutions by pulp fibers were obtained by methods involving direct titration. To obtain further evidence, a few measurements were also made involving

the determination of the electrical conductivity of dilute sodium hydroxide solutions before and after being in contact with pulp fibers. It was found that the conductivity of the alkali solutions decreased on being in contact with the pulp fibers, but in the case of the very dilute solutions, it was quite difficult to obtain an accurate measure of the loss in alkalinity, due to materials present in the pulp which are soluble in the solutions and have an effect on the conductivity. However, this disturbing factor could be roughly accounted for, by measuring the conductivity of distilled water after being in contact with the pulp fibers, and deducting this conductivity value from the conductivities of the pulp-treated alkali solutions. In this manner, the loss in conductivity of sodium hydroxide solutions due to contact with pulp fibers was determined, and the percentage losses in conductivity were found to be of approximately the same order of magnitude as the loss in alkalinity by methods involving direct titration. The results of these measurements are more fully described in the experimental part of this paper.

A few measurements were also made on the loss in hydroxyl ion concentration of dilute sodium hydroxide solutions on contact with pulp fibers. The hydroxyl ion concentrations were determined by a method based on the catalytic decomposition of nitrosotriacetamine. The loss in hydroxyl ion concentration was also found to be of the same order of magnitude as the loss in total alkalinity as determined by direct titration.

THE ACTION OF PULP FIBERS ON DILUTE SODIUM ABIETATE SOLUTIONS

At the concentrations of the beater, the rosin size is hydrolyzed only to a minor extent, and the major portion of a neutral size could be present in the beater as sodium resinate providing there are no factors which affect the slight hydrolytic alkalinity of the solution. The stability of dilute sodium resinate solutions is very largely dependent on the hydrolytic alkalinity. If this alkalinity is removed or neutralized the soap will undergo further hydrolysis until equilibrium conditions are established.

In the previous section the pronounced activity of pulp fibers toward lowering the alkalinity of dilute alkaline solutions was discussed. In very dilute solutions a very large portion of the available alkalinity is removed by the presence of the pulp fibers. The percentage lowering of the alkalinity by the fibers appears to approach 100 percent as the dilution of the alkaline solution increases. Commercial pulp fibers differ from one another in their activity toward lowering the alkalinity of these solutions. In the case of dilute rosin soap solutions, the alkalinity of the solution is probably also reduced by the contact with the pulp fibers. But as the alkalinity is reduced, the soap solution will become unstable and further hydrolysis will take place to make up for the loss in alkalinity and reestablish the necessary equilibrium conditions. Since the various commercial pulp fibers differ from one another quite markedly in their activity toward the alkalinity, it is quite probable that the extent to which the hydrolysis of the soap is forced by the action of the pulp fibers, will depend upon the nature and activity of the pulp fibers.

The action of various commercial pulp fibers toward dilute sodium resinate solutions is illustrated in Figures 10 and 11. These curves were obtained by allowing the pulp fibers to stand in contact with the dilute rosin soap solutions for a period of twenty-four hours, filtering off the fibers and extracting the fiber mats with ether after they were dried. In a few cases the amount of rosin left in the solutions was determined. In these figures, the percent rosin retained by the pulp fibers (the ether extract corrected for the ether solubility of the blank pulp) is plotted against the percentage of sodium resinate present in the solution based on the weight of the pulp. It is quite probable that the rosin found in the pulp fibers is primarily free rosin.

The pulps used in obtaining the curves in Figure 10, were the same as those used in obtaining the alkali removal curves in Figure 9. The action of the pulp fibers on the dilute sodium resinate solutions appears to be quite similar to the behavior of these pulp fibers toward dilute sodium hydroxide solutions. In both cases, the order of activity of the various pulp are the same; the unbleached sulphite samples retained the largest amount of rosin and also exhibits the greatest activity toward alkali solutions while the rag-hardstock shows the lowest rosin retention and also the lowest activity toward the alkali solutions. Since the various pulps are arranged in the same order in both cases, it is quite probable that the pulp fibers force the hydrolysis of the rosin soap, and the rosin found in the fiber mats is the liberated free abietic acid. In the case of the very dilute sodium res-

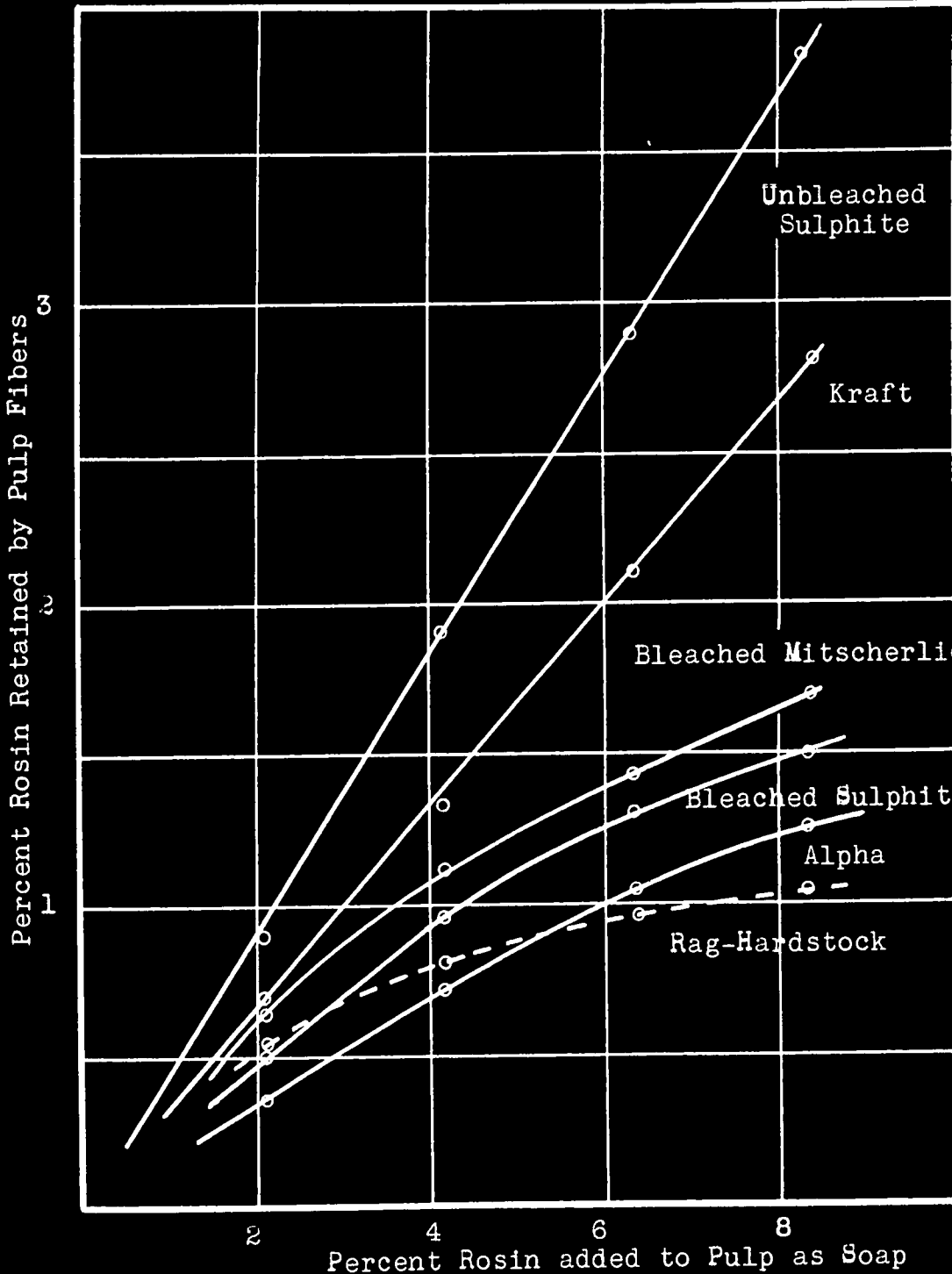


Fig.10. The Action of Commercial Pulp Fibers on Dilute Rosin Soap Solutions

Percent Rosin Retained by Pulp Fibers

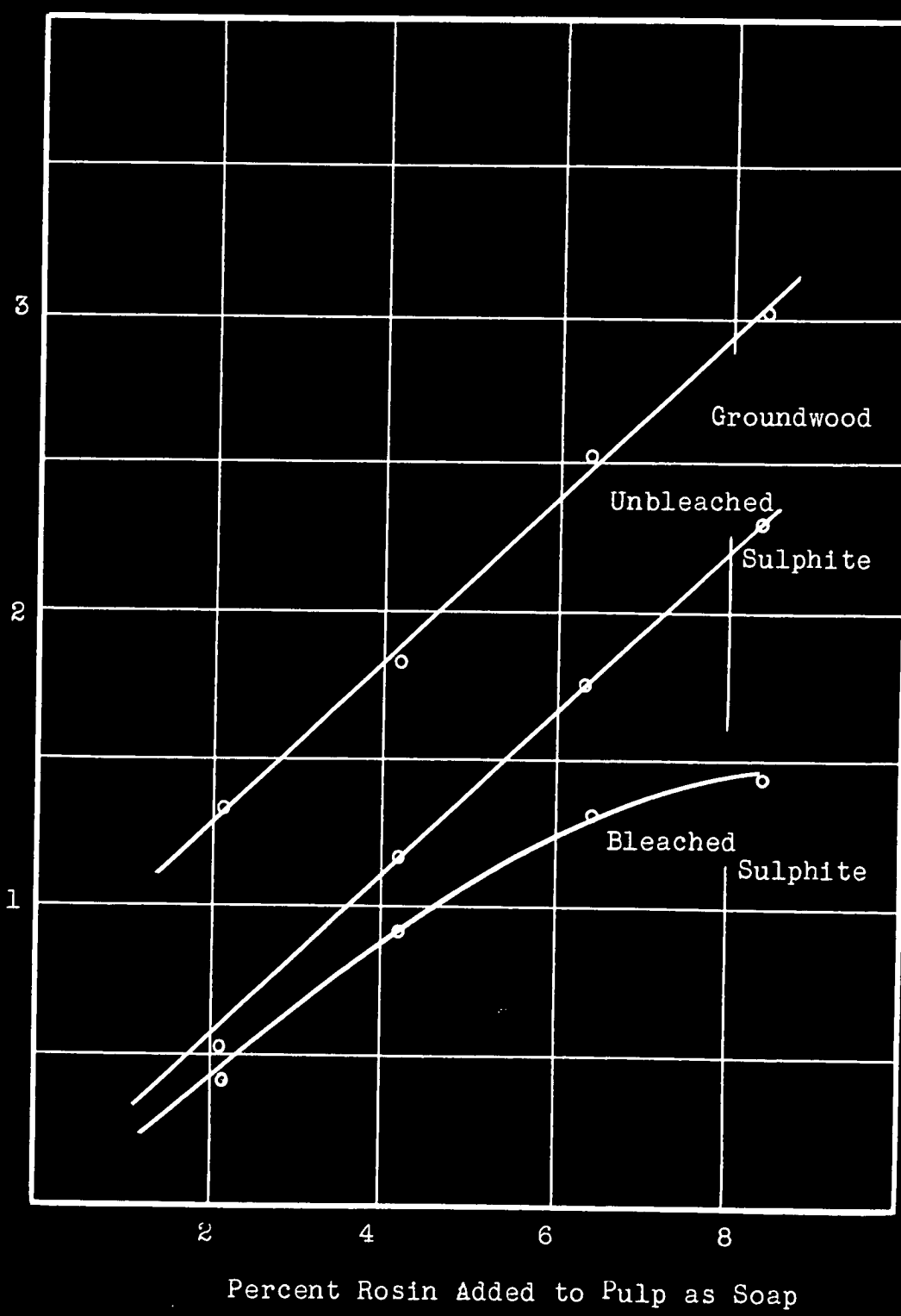


Fig.11. The Action of Commercial Pulp Fibers on Dilute Rosin Soap Solutions

inate solutions, a relatively large portion of the alkalinity is removed by all of the various fibers, and the solutions must be rendered very unstable; but with the exception of the rag fibers, it was possible to distinguish between the activity of the various pulps down to a concentration of $N/500$ sodium resinate.

From these results, it does not necessarily follow, that all pulps of the same class behave the same in this respect. Figure 11 shows the results obtained by using a different sample of unbleached sulphite, and another sample of bleached sulphite. But in general, it seems that the cellulosic purity of the pulp fibers roughly determines the activity of the fibers toward sodium hydroxide and resinate solutions. The order in which the various pulps are arranged is approximately the same as the order of ease of sizing, set up by general experience. In general, rag-hardstock is more difficult to size than alpha fiber, and the latter is more difficult to size than ordinary bleached pulps.

The free rosin liberated by the pulp fibers under these conditions, most likely differs in physical nature from the free rosin present in prepared free rosin sizes. The former is liberated under slowly changing conditions, so that particle size of this colloidal rosin is very small immediately after liberation. The free rosin particles in a prepared free rosin size are probably much larger due to the methods of preparation.

The pulp fibers in the beater, therefore, have a tendency to force the hydrolysis of the rosin size. Under normal conditions, the natural hydrolysis of the size may proceed up to 10 to 15 percent. The presence of the pulp fibers may force the hydrolysis up to 60 percent or higher depending on the pulp and the beater

conditions, but in most cases there is still present in the beater some sodium resinate before the alum is added, providing hard water conditions do not produce complete coagulation. In many cases, the presence of resin soap can be detected in the beater white water, by acidulating with mineral acid or with alum.

EXPERIMENTAL-

Preparation of Abietic Acid:-

Seven hundred grams of white rosin (WW or WG grades) in small lumps, were boiled with 500 cc. of 98 percent acetic acid under a reflux condenser for a period of three hours. The mixture was then filtered while hot through a large plaited filter paper and the filtrate cooled to room temperature or lower. A few crystals of abietic acid were added to start the crystallization or, when none were available, the solution was allowed to stand overnight, where by spontaneous crystallization took place. The product was then filtered on a Buchner funnel using suction, and the filtrate set aside for a second crop. The material on the filters was sucked as free from mother liquor as possible, and washed with successive portions of cold 85 percent ethyl alcohol until the filtrate was practically colorless. The product was again boiled with acetic acid under reflux, cooled, crystallized, filtered and washed as previously described. The product was then crystallized three times from absolute ethyl alcohol and air dried.

Acid Number:-

The acid number was determined by dissolving exactly one gram of the sample in 125 cc of 95 percent ethyl alcohol, and titrating with standard N/10 sodium hydroxide solution, using phenolphthalein as indicator. The acid value (milligrams of sodium hydroxide required to neutralize one gram of acid) was found to be 132.1 as compared to the theoretical value of 132.4. Assuming a monobasic acid, the molecular weight calculated from the above data is 302.9.

as compared with generally accepted value of 302.3 for the molecular weight of abietic acid.

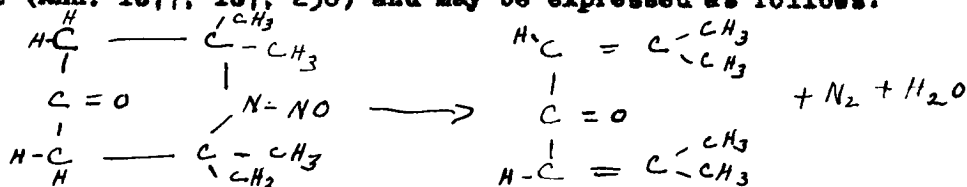
Preparation of Standard Sodium Abietate Solutions:-

An N/10 solution of sodium resinatate was prepared by dissolving 30.23 grams of the acid in 500 cc of .2000 N sodium hydroxide solution and then diluting to exactly one liter. A clear solution with a red brown color was obtained. Solutions of lower concentration were prepared by carefully diluting this stock solution. Solutions of N/100 concentration and below are slightly turbid and opalescent even at room temperature.

The Determination of the Hydrolysis of Sodium Abietate

In the presence of alkali, nitrosotriacetoneamine is quantitatively decomposed into the unsaturated ketone, phorone, with the evolution of nitrogen gas. This decomposition was observed by

Heintz (Ann. 1877, 187, 250) and may be expressed as follows:



Clibbens and Francis (J.C.S. 1912, 101, 2358) made a careful study of this reaction and found the same to be monomolecular, and also found that over a certain range of hydroxyl ion concentration the rate of catalysis is directly proportional to the hydroxyl ion concentration. The course of the reaction could be followed by measuring the volume of nitrogen gas evolved, or by recording the pressure of the same. The former method was employed in the original studies. The apparatus used by Clibbens and Francis was similar to that described by Walton (Z. physik. Chemie 1904, 47, 185) in the latter studies on the catalysis of hydrogen peroxide

by iodine. The reaction was generally carried out in a Jena glass flask, which had an arrangement in the neck to hold one of the reactants in a dropping tube until it was desired to start the reaction. For very dilute solutions of alkali, a silver reaction flask and dropping tube were employed. It is necessary to agitate the contents of the flask, to insure immediate liberation of the gas; this is usually accomplished by shaking the entire flask. The reaction vessel was connected to a gas burette by means of capillary glass tubing. The aqueous solution of the alkali was contained in the dropping tube, but in some cases this procedure was reversed. The flask was set up and shaken in a constant temperature bath and the gas burette was held in a constant temperature jacket.

Francis and Geake (J.C.S. 1913, 193, 1722) investigated the catalytic decomposition of nitrosotriacetoneamine using Barium hydroxide, sodium hydroxide, potassium hydroxide, phosphates tetraethyl ammonium hydroxide, and tetramethyl ammonium hydroxide. The measurements were made by the volume method similar to that used by Clibbens and Francis. For all these various bases and salts, it was found that the rate of the catalytic decomposition was a function of the hydroxyl ion concentration. The rate of decomposition of the amine was found to be directly proportional to the hydroxyl ion concentration up to an hydroxyl ion concentration of .05 N. Above this hydroxyl ion concentration the reaction is still monomolecular, but the reaction constants commence to "drift", that is, the reaction constant is no longer directly proportional to the hydroxyl ion concentration. The method is therefore available for the estimation of the concen-

tration of hydroxyl ion up to a concentration of .05 normal, to a degree of accuracy of 2-3%. The importance of the method as a means of determining the hydroxyl ion concentration lies in the fact, that the effect of neutral salts in ordinary concentration is unimportant.

Francis, Geake, Roche (J.C.S. 1915, 107, 1651) describe a new apparatus for measuring the concentration of hydroxyl ions, based on the catalytic decomposition of nitrosamine, which involves the measurement of pressure rather than volume. With this apparatus the authors were able to obtain results on the hydrolysis of sodium carbonate in good agreement with those obtained by conductivity and electromotive force measurements. They also investigated the use of various other amines, and by using nitroso-vinyl-diacetonamine or nitroso-isobutyl-diacetonamine they were able to bridge the region of ionic concentration which owing to the drift in the constants, cannot be measured through the agency of nitroso-triacetonamine. In the case of nitroso-triacetonamine, the reaction constant commences to drift at a hydroxyl ion concentration of .05 N. For nitroso-vinyl-diacetonamine and nitroso-isobutyl-diacetonamine the reaction constant does not drift until a hydroxyl ion concentration of 0.4 is attained.

Broensted and King (J.A.C.S. 47, 2523, 1925) in their studies on the secondary kinetic salt effect, investigated the catalytic decomposition of nitroso-triacetonamine by hydroxyl ions. They describe another piece of apparatus which was designed to measure quite generally the velocity of a reaction in which a gas is evolved, by a measure of the pressure above the solution as the

reaction proceeds. This apparatus is essentially a modification of that described by Walton (see above) with a manometer to measure the pressure above the solution, instead of measuring the volume of the evolved gas with a burette. The reaction vessel is shaken in a thermostat by means of a special cam arrangement.

Kilpatrick (J.A.C.S. 48; 2091, 1926) in his work on catalysis in buffer solutions, also investigated the catalytic decomposition of nitrosotriacetoneamine. This investigator employed a method of following the course of reaction, involving a measurement of the volume of the gas evolved, but instead of agitating the entire flask, the solution is agitated by means of a stirrer with a mercury seal. The rates of the reaction and the temperature coefficients were determined from 20 to 80 deg. C. It was also found that the temperature coefficients were unaffected by neutral salt and the author finds his results in agreement with Bronsted's concept of secondary salt effect. Bronsted and King were able to show a salt effect for an 0.01 N sodium hydroxide solution at 15 deg. C amounting to 7 percent in an 0.1 N salt solution.

The apparatus used for this work was similar to that used and described by Francis (see above), involving the measurement of the volume of nitrogen gas evolved. A sketch of the apparatus is given in Figure 12. The reaction vessel A was a 100 milliliter pyrex volumetric flask, which was connected to the gas burette C by means of the capillary glass tubing B. An effective joint between the flask and the capillary tubing was attained by the use of a short piece of rubber tubing of the proper dimensions, which was slipped over the end of the capillary tubing and then forced tightly into the neck of the reaction flask. A similar

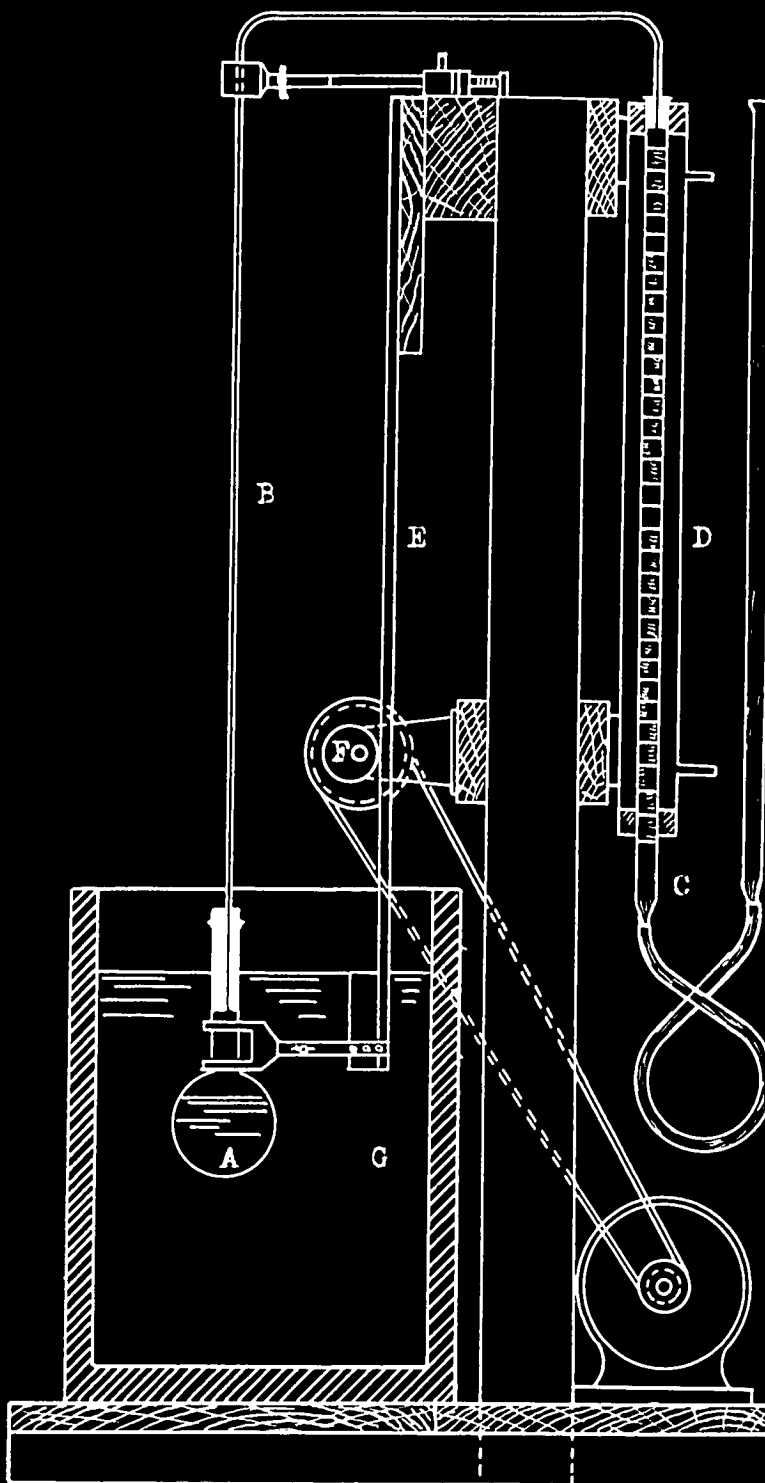


Fig. 12

joint was made between the capillary tubing and the burette. The flask is held in a clamp attached to the vertical wooden shaft E. This shaft is attached firmly at the upper end, but the lower end was capable of vibrating through a lateral distance of about two or three centimeters. The vibration was produced by means of a cam arrangement on a horizontal shaft driven by a small electric motor, as shown in the diagram. The speed of the shaft driving the cam was 350 R.P.M. This produced a very violent and effective agitation in the reaction flask, which was only filled to three quarters of its total capacity. The vertical length of the capillary glass tubing B was about three feet, and it was sufficiently elastic to withstand this vibration. The reaction vessel was held in a constant temperature water bath, which could be held within .02 deg. C. The gas burette C is inclosed in a constant temperature water jacket, the water for the same was circulated through another thermostat.

The nitrosotriacetoneamine used for this work was obtained from the Eastman Kodak Research laboratory, and the quantity of nitrogen liberated from a given amount of chemical was within one percent of the theoretical value.

The Procedure for making the determination was briefly as follows: 50 cc. of the alkali or soap solution were accurately pipetted into the reaction flask, and the flask was then shaken until thermal equilibrium was attained. A solution of the nitrosotriacetoneamine (containing about six grams of amine per liter) was also kept in the thermostat and brought to thermal equilibrium. In the case of the soap solutions, which developed considerable foam due to the agitation, a few drops of kerosene were added to

eliminate the possibilities of foam getting into the capillary tubes. When it was desired to start the reaction, 25 cc. of the amine solution were carefully measured off with a pipette and run into the reaction flask, the flask was then immediately connected to the delivery tubes, and the agitation started. Volume readings are taken at suitable intervals depending on speed of the reaction. The time intervals were measured with a stop watch; in nearly every case, with the exception of exceedingly slow reactions the decomposition was allowed to go to completion. In the case of the very slow reactions the final volume was obtained by liberating and measuring the nitrogen from the same quantity of the same nitrosamine solution with a stronger alkali.

For a monomolecular reaction, the velocity of the same is given by the following equation:

$$k = \frac{1}{t} \ln \frac{a}{a-x}$$

where k is the velocity constant, a is the quantity of reactive constituent present at zero time, x is the quantity of reactive constituent converted in time t , and $a-x$ is the quantity of reactive constituent remaining at time t . This equation can be more conveniently expressed in terms of burette readings as follows:

$$k = \frac{1}{t} \ln \frac{V_{\infty} - V_0}{V_{\infty} - V_x}$$

where V_{∞} is the final burette reading. V_0 the initial burette reading, and V_x is the reading at any particular time t . The following is a typical experimental run:

The reaction flask contained .200 gram of amine, 50 cc. of water

4 drops of kerosene, and 25 cc. of .0150 N NaOH.

Temperature maintained at 55.8 deg. C.

Minutes	Reading V	$V_a - V_x$	$\frac{V_x}{V_a - V_x}$	$\ln \frac{V_x}{V_a - V_x}$	k
0.0	2.5	0.0	24.95	1.00	0
7.0	12.90	10.40	14.55	1.715	.540
8.0	14.00	11.50	13.45	1.855	.618
9.0	15.05	12.55	12.40	2.012	.700
10	16.00	13.50	11.45	2.185	.782
11.5	17.20	14.70	10.25	2.435	.890
13	18.35	15.85	9.10	2.745	1.010
15	19.67	17.17	7.78	3.21	1.17
17	20.80	18.30	6.65	3.75	1.322
19	21.80	19.30	5.65	4.42	1.485
22	22.90	20.40	4.55	5.48	1.70
25	23.80	21.30	3.65	6.84	1.92
30	24.90	22.30	2.55	9.79	2.28
180	27.45	24.95			Average
					.0775

In order to check the apparatus and the procedure employed, a series of experiments was carried out using dilute sodium hydroxide solution of known strength. The following table gives a few data for the reaction constant at several concentrations of sodium hydroxide, together with the values of k/NaOH and k/OH . These values were obtained at 29.8 deg. C.

Normality NaOH	Normality OH	k	k/NaOH	k/OH
.0100	.0096	.0178	1.78	1.85
.0100	.0096	.0183	1.83	1.91
.0200	.0190	.0357	1.78	1.88
.0300	.0282	.0523	1.74	1.85
.0200	.0190	.0352	1.77	1.86
			Average	1.87

The k/OH value obtained by Francis at 30 deg. was 1.91 and that reported by Kilpatrick at the same temperature was 1.89.

The Extent of the hydrolysis of N/100 sodium abietate solution was then determined at 30 deg. C. The complete data for one of these determinations are as follows: The reaction flask contained .2000 gram of amine, 50 cc. of water, 4 drops of kerosene, and 25 cc of .030 N sodium abietate. The reaction proceeded at a temperature of 29.8 deg. C.

Minutes	Reading	V	$V - V_\infty$	$-\frac{V_\infty}{V - V_\infty}$	ln	k
0	1.10	.00	28.50	1.000	-	-
135	1.53	.43	28.07	1.016	.0159	.000118
210	1.74	.64	27.86	1.024	.0237	.000113
400	2.20	1.10	27.40	1.040	.0393	.000098
425	2.25	1.15	27.35	1.042	.0412	.000097
550	2.67	1.57	26.93	1.058	.0564	.000103
870	3.40	2.30	26.20	1.089	.0854	.000098
1210	4.20	3.10	25.40	1.122	.1150	.000095
1270	4.34	3.24	25.26	1.130	.1250	.000099
1330	4.59	3.49	25.01	1.140	.1338	.000100
1450	4.75	3.65	24.85	1.147	.1371	.000096
1525	5.00	3.90	24.60	1.158	.1468	.000096
1585	5.06	3.96	24.54	1.163	.1510	.000095
1645	5.18	4.08	24.42	1.172	.1590	.000097
		28.50			Average	.000100

The hydroxyl ion concentration may then be estimated by taking the hydroxyl ion constant from above as 1.87 and calculating as follows:

$$.000100 / 1.87 = .000054 \text{ N OH ion.}$$

The percent hydrolysis of the N/100 sodium abietate solution at 29.8 deg. C is then found to be -

$$.000054 \times 100 / .01 = 0.54 \text{ percent}$$

The average value of the percent hydrolysis of N/100 sodium resinate from several similar determinations was found to be 0.50 percent. This value appears to be of the proper order of magnitude when compared with the value of 5.7 percent for an N/100 sodium resinate solution at 90 deg. C., obtained by Beedle and Bolam (J. Soc. Chem. Ind. 40; 4, 27F, 1921). Due to the apparently slight hydrolysis of the resinate solutions, and the velocity of the decomposition of the nitrosotriacetoneamine at 30 deg. C. it is rather difficult to measure the hydrolysis of more dilute solutions. However, the above data seems to indicate that the hydrolysis of the soap does not proceed to a very appreciable extent in the concentrations prevailing in the beater. In order to determine the degree of hydrolysis of more dilute sodium resinate solutions, it was found necessary to resort to a more elevated temperature, where the velocity of the reaction is considerably greater and the extent of the hydrolysis is also greater.

A series of experiments was then carried out using dilute sodium hydroxide solutions of known strength, in order to obtain the hydroxyl ion constant of the reaction at this temperature. The reaction were carried out at 55.8 deg. C. which corresponds to 133 deg. F. The following table shows the reaction constant at several alkali concentrations at this temperature, together with the values of k/OH . For these very dilute solutions at this temperature, the degree of ionization was taken as one hundred percent.

Normality of NaOH	k	k/OK
.00200	.0294	14.7
.00200	.0280	14.0
.00300	.0459	15.3
.00500	.0752	15.0
.00500	.0772	15.4
.00366	.0560	15.3
	Average	15.0

The value calculated from the data reported by Kilpatrick (J.A.C.S. 48; 2091, 1926), for this particular temperature was found to be 14.9. For these very dilute solutions of sodium hydroxide, the presence of small amounts of carbon dioxide has an appreciable effect. The solutions had to be prepared from freshly redistilled water which was boiled just prior to making up the solutions. The experiments had to be carried out immediately after preparing the solutions.

The extent of the hydrolysis of an .0033 N sodium abietate solution was then determined. The complete data for one of these determinations are as follows: The flask contained .200 gram of amine in 50 cc of freshly boiled distilled water, 4 drops of kerosene, and 25 cc of .0100 sodium resinate solutions. The reaction proceeded at a temperature of 55.8 deg. C. The temperature of the water in the gas burette jackets was held at 22.5 deg. C. throughout the experiment.

Minutes	Reading	V	$V_a - V_x$	$\frac{V_a}{V_a - V_x}$	ln	k
0	.80	0	26.40	1.00	-	-
30	2.68	1.88	24.52	1.078	.0752	.00250
45	3.50	2.70	23.70	1.114	.1080	.00240
75	5.08	4.28	22.12	1.194	.1775	.00237
168	9.30	8.50	17.90	1.475	.3820	.00227
186	10.00	9.20	17.20	1.535	.429	.00231
360	15.38	14.58	11.82	2.23	.802	.00223
420	16.74	15.94	10.46	2.525	.936	.00223
1170	25.10	24.30	2.10	12.57	2.74	.00234
1265	25.73	24.93	1.47	17.96	2.89	.00237
1410	26.15	25.35	1.05	25.10	3.22	.00228
	27.20	26.40				
Average						.00231

The hydroxyl ion concentration of this soap solution may then be calculated from this value and the hydroxyl ion constant-

$$.00231 / 15.0 \text{ ----- } .000154$$

and the percent hydrolysis of the .00330 N sodium abietate solution may then be estimated as:

$$.000154 \times 100 / .0033 \text{ ----} 4.7 \%$$

The average value of the percent hydrolysis of N/300 sodium abietate solution at 65 deg. C. was found to be 4.3%. This value also appears to be of the proper order of magnitude when compared with the figure, 0.50% for the hydrolysis of N/100 sodium resinate at 30 deg. C, previously obtained, and the results obtained by Beedle and Bolam. These results indicate that under ordinary beater conditions, the natural hydrolysis of sodium resinate does not proceed to any appreciable extent, and that if there were no other disturbing factors, such as impurities in the water and the effect of the pulp on the soap, a predominant percentage of the size could exist as sodium resinate. The conductivity measurements described below, also seem to indicate

that the extent of the natural hydrolysis of sodium resinate is not very appreciable at concentrations prevailing in the beater.

An experiment was made in an attempt to discover the effect of the presence of pulp fibers on the hydroxyl ion concentration of dilute sizing solution. The procedure was as follows: Four grams of bleached sulphite pulp were thoroughly mixed with one hundred cc. of an 0.01 N sodium resinate solution and allowed to stand two hours. The pulp fibers were then filtered off, and twenty-five cc. of the filtrate were used in the catalysis apparatus. The reaction flask contained .200 gram of amine in 50 cc. of water and the 25 cc. of the above filtrate. The experimental conditions were exactly the same in the previously described hydrolysis experiment, with the exception that in this case the soap had been in contact with pulp fibers. The hydroxyl ion concentration was found to be .000054 N. This indicates an appreciable lowering of the hydroxyl ion concentration, since the hydroxyl ion concentration of the untreated solution was found to be .000154 N, as given above. Apparently the presence of the pulp fibers lowered the hydroxyl ion concentration by about sixty percent, which in turn should have an appreciable effect on the extent of the hydrolysis of this soap solution. The effect of a large portion of the original hydroxyl ion concentration is removed by the presence of the pulp either by a process of sorption by the fibers, or by a neutralization due to impurities in the pulp, or a combination of these processes. The removal of the alkali by the pulp should tend to disturb the normal hydrolysis equilibrium of the sodium resinate and should force the hydrolysis to an extent depending, along with other

factors, on the amount of alkali removed. The behavior of various pulps toward dilute sodium hydroxide solutions has been studied with the intention to ascertain the effect of this alkali removal on the sodium resinate solutions; and will be described later.

THE CONDUCTIVITY OF SODIUM RESINATE SOLUTIONS-

Dilute solutions of sodium abietate, N/100 and below, show a slight turbidity even at room temperature, and this turbidity increases gradually with rising temperature. Solutions having a concentration greater than N/100 appear to be perfectly clear and homogeneous. The concentration at which the turbidity appears is not definite and sharply defined, but at room temperature the effect is noticeable in the range of N/100 solution. Freshly prepared solutions are opalescent, but on standing or with rise in temperature the colloidal particles seem to coalesce and gradually become quite coarse and finally settle out. From rough qualitative observation, the amount of material responsible for this turbidity appears to be only a small fraction of the total resin present, since on the addition of dilute mineral acid a comparatively large floc is produced. This would be expected in the light of the previously described work in the extent of the hydrolysis, for at room temperature, the turbidity of an N/300 sodium resinate solution must be due to less than five percent of the total resin present. In these dilute solutions, the course of the hydrolysis may proceed according to the generally accepted reaction-



where R is the abietic acid radical, and the abietic acid HR, is present in a colloidal condition; or the reaction may proceed the following course as suggested by McBain-



where the acid soap is in suspension, either course or colloidal as the case may be, and consists of something between the neutral salt NaR and the acid soap NaHR₂. Probably in these very dilute solutions, the formation of the acid soap does not proceed to any great extent, and the hydrolysis primarily follows equation (1). In either case, any great changes in the equilibrium due to dilution should be reflected in the conductivity curves of these solutions.

A few measurements were made on the electrical conductivity of sodium abietate solutions of concentrations ranging between N/10 and N/500. The apparatus employed consisted of an ordinary, Arrhenius type, conductivity cell with platinized platinum electrodes, and a small potentiometer used as a Wheatstone Bridge. An alternating current with a frequency of one thousand cycles was used. The solutions were prepared separately rather than by dilution in the cell. For comparison, measurements were also made on dilute sodium hydroxide solutions in the same concentration range. The following tables show the results obtained for the specific and equivalent conductances of sodium hydroxide and resinate solutions at 25 deg. C.

Sodium Abietate Solutions

Concentration	Specific Conductance	Equivalent Conductance
.002 N	.000153	76.5
.004	.000296	74.2
.006	.000437	73.2
.008	.000565	70.6
.010	.000685	68.5
.0557	.00282	50.7
.1113	.00508	45.7

Sodium Hydroxide Solutions

Concentration	Specific Conductance	Equivalent Conductance
.00135 N	.000330	245
.00364	.000895	245
.00548	.00135	245
.00756	.00184	244
.00944	.00228	242

The specific conductances are plotted in figure 1, and figure 2 shows the trends of the equivalent conductances of the hydroxide and resinate solutions. The equivalent conductance of sodium hydroxide at infinite dilution obtained by extrapolation from these data is 246 as compared with the accepted value of 243. The equivalent conductance curve for sodium hydroxide is almost horizontal in this concentration range, while that of the sodium abietate increases slightly with increasing dilution. The conductivity of the sodium resinate is rather high, but soap solutions in general have abnormally high conductivities. From the above data, the apparent conductivity (equivalent) at infinite dilution of the sodium abietate is about 90; although the approximation of this value by extrapolation is quite unreliable, it is interesting to compare this figure with the equivalent conductance of sodium acetate at infinite dilution, which is 92 at 25 deg. C.

The equivalent conductance of the resinate solutions increase slightly with increasing dilution, but the slope of the curve is not particularly abnormal, which seems to indicate, that no great fundamental changes are taking place in the constitution of the electrolyte. The extent of the hydrolysis undoubtedly increases with increasing dilution, nevertheless the rate at which this change increases through out the particular concentration range under consideration, is not very rapid.

Determinations of the hydroxyl ion concentration of sodium resinate solutions based on the catalytic decomposition of nitrosotriacetoneamine, indicate that the extent of hydrolysis of an N/300 solution is somewhat less than 5 percent at 56 deg C, and that the hydrolysis of an N/100 sodium resinate solution is about .5 percent at 30 deg. C. The conductivity measurements seem to indicate that no great changes are taking place in the constitution of the electrolyte in the concentration range between N/100 and N/1000. The extent of the hydrolysis of the soap apparently does not increase very rapidly on dilution over this concentration range, and is probably less than ten percent in soap concentrations below N/1000. The concentration of rosin size under beater conditions ranges from N/1000 to N/100, assuming a neutral size. At beater concentrations, therefore, the extent of the normal hydrolysis of the rosin soap is not very great, and probably less than 10 percent under most conditions. Providing there are no factors which would tend to force the hydrolysis of the soap, the bulk of the size added to the beater as sodium resinate can exist as the true soap, with the formation of only a rather small percentage of hydrolyzed and colloidal resin. Commercial pulps, however, have a tendency

to greatly reduce the alkalinity of dilute alkali solutions, and this behavior will have an appreciable effect on the sizing solutions. This behavior will be discussed in the following pages.

In the previously described measurements on the hydrolysis of sodium abietate solutions, it was found that the hydroxyl ion concentration of the soap solution was considerably diminished by being in contact with commercial pulp fibers. It was also observed that when pulp fibers were allowed to stand in contact with dilute sodium resinate solutions for several hours and subsequently filtered off to give a clear filtrate, the amount of abietic acid that could be precipitated from the filtrate by a mineral acid was less than the precipitate obtained from a similar solution that had not been in contact with the pulp. This latter observation might suggest that the sodium soap, which has a large unsaturated molecule, is sorbed as such by the cellulose fiber interface. However, the fact that cellulose has a tendency to pick up alkali, and that the hydroxyl ion concentration of a soap solution is reduced by the presence of pulp fibers, with a lowering in concentration of the soap solution, indicate the probability of the pulp fibers forcing the hydrolysis of the sodium resinate, with the liberation of appreciable quantities of colloidal abietic acid. This abietic acid is in an extremely fine colloidal condition when it is first liberated and could be readily sorbed or mechanically held by the pulp fibers. The tendency of pulp fibers to lower the alkalinity of dilute alkali solutions appears to be of fundamental importance to the problem of rosin sizing, and for this reason a study was made of the behavior of various commercial pulps toward dilute alkali solutions.

This study was limited to alkali concentrations which would approximate the conditions prevailing in the beater, that is, to solutions which contain amounts of alkali as sodium hydroxide equivalent to the amounts of sodium resinate in the beater water. These concentrations range between N/100 and N/1000. The lowering of the alkalinity of solutions by the presence of pulp fibers was determined by three independent methods; the first method involved direct titration, the second conductivity measurements, and the third method was based on the estimation of the hydroxyl ion concentration by the rate of the catalytic decomposition of nitrosotriacetoneamine. The first method is the simplest and was used throughout, the others were used for verification in a few cases.

In a preliminary experiment, the following procedure was chosen: Ten-gram samples of shredded pulp were placed in Erlenmeyer flasks, of 500 cc. capacity. To each of these was added a 250 cc. portion of an alkali solution, which gives a consistence of 4 percent. A series of samples was thus prepared, with alkali solutions ranging from .002 N to .01 N NaOH at intervals of .002 N. A portion of each of the alkali solutions was kept for a blank determination. The mixture in the flasks were thoroughly shaken and then kept in a water bath at 20 deg. C. for a period of twenty-four hours. At the end of this period the fibers were filtered off on a bare Buechner funnel. The filtrates were poured through the mat a second time to give a clear solution. The alkali concentrations were then determined by titrating with N/100 standard sulphuric acid solution using phenolphalein as an indicator. Several titrations were carried out with hot solutions to remove the effect of carbon dioxide with this indicator; the differences

in titer between the filtrates and the blank solutions is a measure of the loss in alkalinity. The following table gives the results of this experiment for two different pulps:

Bleached West Coast Sulphite (Hemlock)

Original Normality	Final Normality	% Drop in Normality	Gr. NaOH removed per gram dry pulp
.00180	.00048	73.2	.00131
.00380	.00160	58.0	.00223
.00580	.00317	45.6	.00266
.00760	.00480	36.8	.00285
.00980	.00653	33.4	.00330

Purified Wood Fiber, Alpha Pulp

.00180	.00127	28.9	.00053
.00380	.00298	21.6	.00084
.00580	.00477	17.8	.00105
.00760	.00658	13.4	.00106
.00980	.00864	11.8	.00119

These data are represented graphically in Figures 3 and 4. In Fig. 3, the percent of the available alkali removed is plotted against the original alkali concentration. In Fig. 4, the weight of sodium hydroxide removed per gram of dry pulp is plotted against the initial concentration. The percent removal of the available alkalinity is very high for the sulphite pulp, especially in the more dilute solutions, and rapidly falls off with increasing concentration. The curve for the purified wood fiber is similar to that of the sulphite pulp, although the removal of alkalinity is very much less than that of the unpurified material. The great differences in the behavior of these pulps seem to indicate that the nature of the pulp is a predominant factor in affecting alkali removal. As already noted, the curves shown in Fig. 4 resemble typical adsorption curves. If the mechanism of this alkali removal were due to true

adsorption, then a greater alkali removal would be favoured by lower temperatures. It will be shown later that this is not the case. It does not seem likely that the loss in alkalinity is due to a neutralization effect, since this would require a rather sharp break in the curve, where the neutralization would be complete. Moreover, these quantities of alkali would require an abnormally high acid content in the pulp.

In the preceding experiment the time of contact of the pulp fibers with the solution was arbitrarily chosen as twenty-four hours. It was necessary to determine the time required for equilibrium conditions to be established, and experiments were made to determine the change in alkalinity of solutions with increase in the time of contact with the pulp fibers. The procedure for making these measurements was as follows: Erlenmeyer flasks of 500 cc. capacity, each containing 10 grams of shredded sulphite pulp, and a 250 cc. portion of a standard sodium hydroxide solution were allowed to stand in a water bath at 20 deg. C. for periods of time ranging from two to seventy-hours. A portion of the standard alkali solution was kept for a blank determination. When the time of contact of the solution with the fibers had elapsed, the fibers were filtered off on a bare Buechner funnel and the filtrate was poured through the mat a second time to obtain a clear solution. The alkalinity of the filtrates and the blank solutions were determined by titrating a 50 cc. aliquot portion of each with standard N/100 sulphuric acid solution, using phenolphthalein as an indicator. The following tables give the results of three series of measurements at different original alkali concentrations. The same pulp was used throughout.

ALKALI REMOVAL WITH TIME AT 20 deg. C. BLEACHED HEMLOCK PULP
CONSISTENCY - 4%

Original Concentration - .00225 N NaOH

Time	Normality	Percent drop in Alkalinity
0	.00225	00
2-3/4 hrs.	.00106	53
5-3/4 "	.000895	60
11-1/2 "	.000750	67
24-1/2 "	.000480	79
48 "	.000310	86
71 "	.000225	90

Original Concentration - .00460 N NaOH.

0	hrs.	.00460	00
2-1/2	"	.00277	40
5-1/4	"	.00252	45
11	"	.00232	50
24	"	.00206	55
47	"	.00186	60
70	"	.00178	61

Original Concentration - .00980 N NaOH

Time	Normality	Percent drop in Alkalinity
0	.00980	00
2-1/2 hrs.	.00690	29.6
5 "	.00670	31.6
11 "	.00650	33.7
24 "	.00636	35.1
47 "	.00616	37.2
70 "	.00605	38.2

In Fig. 5, The percent of available alkalinity removed is plotted against the time of contact of the pulp with the solutions. In the case of the .00225 Normal series, equilibrium conditions are not attained even after seventy hours of contact, the curve still has an appreciable slope at this point. In the .0046 Normal series, an equilibrium is very nearly attained after seventy hours, and in the .0098 Normal series the curve is practically horizontal

after this period of contact. In every case, the rate of the loss in alkalinity is very rapid in initial hours of contact; the rate of removal being rapid in the strong solutions.

THE EFFECT OF TEMPERATURE ON ALKALI REMOVAL. The curves obtained in the preliminary experiments (Fig. 4) resemble typical adsorption curves. As already noted, if the mechanism of the alkali removal were due to a process of true adsorption, lower temperatures would favour a greater removal of alkali, other conditions being the same. To check this point, two series of experiments were carried out, one at 20 deg. C and the other at 40 deg. C. Since the time of contact was found to be an important factor in determining the drop in alkalinity, the effect of temperature could be most readily observed by determining the loss in alkalinity with time at these two temperature, using the same initial alkali concentration in both series. The procedure for making these measurements was the same as that used in the previously described experiments on the removal of alkali with time. The original concentration of the sodium hydroxide solution was .0050 Normal and the consistence of the pulp fibers was 4 percent. One set of flasks was kept in a bath at 20 deg. C; and the other set in a thermostat at 40 deg. C. The pulp used in these series was a bleached sulphite pulp from Western Hemlock.

ALKALI REMOVAL WITH TIME AT 20 deg. C. Bleached Hemlock Pulp.
CONSISTENCY - 4%

Original Concentration - .00500 N NaOH

Time	Normality	Percent drop in Alkalinity
0	.00500	00
2 hrs.	.00322	35.6
4 "	.00288	42.4
8 "	.00248	50.4
16 "	.00233	53.4
28-1/2 "	.00216	56.8
64 "	.00189	62.2

ALKALI REMOVAL WITH TIME AT 40 deg. C. Bleached Hemlock Pulp.
CONSISTENCY - 4%

Original Concentration - .00500 N NaOH

Time	Normality	Percent drop in Alkalinity
0	.00500	00
2 hrs.	.00259	48.2
4 "	.00217	56.6
8 "	.00193	64.4
16 "	.00166	66.8
30-1/2 "	.00149	70.2
66 "	.00116	76.8

In Fig. 6, the percent of the available alkalinity removed is plotted against the time of contact at these two temperatures. Both curves have the same general form, a larger percentage of the available alkalinity is removed at the higher temperature, and the curves appear to diverge slightly as the time of contact of the pulp with the solutions increases. The removal of the alkali, therefore, cannot be due to a true mechanism of adsorption, and is probably a rather complex process, depending on the nature of the constituents present in the pulp, such as beta and gamma celluloses, pentosans, lignin residues, etc. The fact that the alkalinity is reduced is our main concern in this study, whatever the actual mechanism of the removal may be.

THE EFFECT OF PULP CONSISTENCE ON THE LOSS IN ALKALINITY. In the previously described measurements, the consistence of the pulp fibers in the solutions was arbitrarily chosen as 4 percent; in every case a pulp suspension was made by adding 10 grams of shredded, air-dry fiber to 250 cc. of solution. A series of measurements was made to determine the loss in alkalinity at various pulp consistencies. Definite quantities of shredded pulp were added to Erlenmeyer flasks of 500 cc. capacity, and to each flask was added a 250 cc. portion of a standard alkali (NaOH) solution, to give consistencies of pulp ranging from one to six percent. The flasks were allowed to stand in a water bath at 20 deg. C. for a period of twenty-four hours. The fibers were then removed by filtering through a bare Buechner funnel, and pouring the filtrate through the mat a second time to obtain a clear solution. The alkalinity of the filtrates and the blank solution were determined as in the previously described experiments. The results of these measurements are given in the following table:

ALKALI REMOVAL AT VARIOUS CONSISTENCIES AT 20 deg. C. Bleached Hemlock Pulp (Sulphite)

Time of contact of solutions with fibers - 24 hours.

Original Concentration of Sodium Hydroxide - .00362 Normal.

Consistency	Normality	Percent drop in Alkalinity
0	.00362	00
1	.00307	15.2
2	.00252	30.3
3	.00204	43.7
4	.00157	56.6
5	.00120	66.8
6	.00101	72.2

These results are shown graphically in Fig. 7. The solid-line curve shows the percent available alkalinity removed at the various consistencies. The slope of this curve changes very little at the lower consistencies, but falls off quite rapidly above a consistency of four percent, where the residual alkali concentration becomes rather low. The broken-line curve shows the milligrams of sodium hydroxide removed per gram of dry pulp at the various consistencies. This curve maintains a maximum of about 2.2 milligrams up to a consistency of about percent, and then gradually drops off with increasing consistency. Apparently, a consistency of about four percent is the most suitable for making determinations on the loss in alkalinity.

THE BEHAVIOR OF COMMERCIAL PULPS TOWARD DILUTE ALKALI SOLUTIONS-

In the preliminary studies of the action of pulp fibers on dilute sodium hydroxide solutions, two widely different pulps were used, namely, an ordinary bleached sulphite pulp and a purified wood fiber pulp. These two pulps have quite different chemical and physical characteristics. The purified wood fiber has a higher alpha-cellulose content and a lower copper number than the ordinary sulphite pulp. Their behavior in the beater is also quite different, the alpha-pulp develops in strength more slowly and is more difficult to hydrate than the sulphite pulp. As is shown in figures 3 and 4 these two pulps differ very widely in their action on dilute sodium hydroxide solutions. In an N/500 sodium hydroxide solution, under similar conditions of time of contact, consistency, etc, the sulphite pulp causes a reduction in alkalinity of the solution of over 75 percent, as compared with a 30 percent reduction in the case of the alpha pulp. In the

range of alkali concentration under consideration, the action of the sulphite pulp is almost three times as great as that of the purified wood fiber. The removal of the alkalinity of solutions by pulp fibers appears to be a rather complex process, and is probably controlled to a great extent by the physical and chemical characteristics of the pulp fibers. Certain chemical constituents present in pulp fibers, such as lignin residues, beta and gamma-cellulose, pentosans and the residual hemicellulose, may influence the behavior of pulp toward dilute alkaline solutions. The removal of the alkali may be partially due to adsorption processes, in which case, the physical condition of the fiber interfaces, the degree of swelling, etc. may play a predominant role. The preliminary experiments indicate that commercial pulps differ from one another toward sodium hydroxide solutions. In the case of dilute sodium resinate solutions, a reduction in the normal alkalinity of the soap would tend to shift the equilibrium conditions and force the hydrolysis of salt. Since the lowering of the alkalinity depends on the nature of the pulp fibers, the extent of the forced hydrolysis of the sizing solution will also be determined by the nature of the pulp fibers. Pulp fibers which have a pronounced activity toward lowering the alkalinity of the beater water, would force the hydrolysis of the soap and consequently change the condition of rosin size from a true molecularly dispersed sodium salt to a colloidal suspension of abietic acid. In the case of a neutral size, the amount of colloidal rosin formed in this manner would be determined by the nature of the pulp fibers. A study was made of the activity of the ordinary types of commercial pulps toward lowering the alkalinity of dilute alkali solutions, to obtain

further information concerning the probable behavior of these pulps on the constitution of sizing solutions.

In order to compare the action of various commercial pulps on dilute alkaline solutions, measurements were made to determine the loss in alkalinity at various sodium hydroxide concentrations, under more or less standardized conditions. The shredded pulp was allowed to stand in contact with the standard sodium hydroxide solutions for a definite period of time, as in the previous measurements. The consistency of the pulp fibers in the solution was 4 percent, and the time of contact of the pulp fibers with the solution was chosen as thirty hours. In the more dilute solutions, it was shown that equilibrium conditions are not attained in this period of time, but longer periods were impractical, and since all the pulps received the same treatment the results are comparable. In every case, ten grams of shredded pulp were shaken with 250 cc of the standard sodium hydroxide solution and allowed to stand in a thermostat at 20 deg. C for thirty hours. The fibers were then filtered off on a bare Buechner funnel, and the filtrate poured through the mat a second time to obtain a clear solution. The alkalinity of the filtrate was determined by titrating a 50 cc aliquot portion with standard N/100 sulphuric acid solution, using phenolphthalein as indicator. The results of these determinations are given in the following tables:-

THE EFFECT OF VARIOUS COMMERCIAL PULPS ON DILUTE SODIUM HYDROXIDE SOLUTIONS

COTTON CELLULOSE PULP-BAG Hardstock.

Original Normality	Final Normality	% Loss in Alkalinity	Milligr. NaOH per gram of Pulp
.00137	.00105	23.4	.32
.00340	.00281	17.3	.59
.00536	.00473	11.8	.63
.00744	.00675	9.3	.69
.00990	.00907	8.4	.83

BLEACHED MITSCHERLICH SULPHITE

.00137	.00017	87.5	1.20
.00340	.00091	73.3	2.49
.00536	.00224	58.2	3.23
.00744	.00377	49.3	3.67
.00990	.00585	40.9	4.05

UNBLEACHED SULPHATE- KRAFT

Original Normality	Final Normality	% Loss in Alkalinity	Milligr. NaOH per gram of Pulp
.00135	.000107	92.0	1.26
.00340	.00083	75.5	2.57
.00566	.00224	60.5	3.42
.00744	.00364	51.1	3.81
.00990	.00572	42.2	4.17

UNBLEACHED SULPHITE

.00140	.000107	92.5	1.30
.00364	.000524	85.5	3.11
.00547	.00118	78.5	4.29
.00755	.00215	71.5	5.40
.00943	.00349	63.0	5.94

BLEACHED SULPHITE- West Coast Hemlock

.00180	.000360	80.0	1.44
.00380	.00141	63.9	2.43
.00580	.00284	51.0	2.96
.00760	.00444	41.6	3.16
.00980	.00635	35.2	3.45

Purified WOOD FIBER - Super Alpha

.00180	.00122	32.0	.576
.00380	.00289	23.9	.91
.00580	.00464	20.0	1.16
.00760	.00639	16.0	1.22
.00980	.00851	13.1	1.28

The above data are represented graphically in figures 8. and 9. In Fig. 8, the percent of the available alkalinity removed is plotted against the original sodium hydroxide concentration, and Fig. 9 shows the milligrams of sodium hydroxide removed per gram of dry fiber for the original alkali concentrations. These curves illustrate the great difference in behavior of typical commercial pulps. All of the pulps studied, give curves of the same general form, which seems to indicate that the mechanism of the alkali removal is the same for all pulps. The unbleached sulphite pulp shows the greatest activity in removing the alkalinity of the solutions. It not only removes the bulk of the alkali in the more dilute solutions, but it also removes a relatively large quantity of the available alkali over the entire range of concentration. The kraft and the bleached Mitscherlich sulphite have very nearly the same activity toward alkali removal, the kraft pulp having a slightly greater action. The particular sample of bleached sulphite used in this study was a pulp of rather high quality, suitable for high grade writings and book paper. The ability of this pulp to remove alkali is appreciably lower than that of the bleached Mitscherlich sulphite. The behavior of the purified wood fiber, the alpha-pulp, is quite different from that of the other chemical wood pulps; its ability to remove alkali is very much lower than the activity of the other wood pulps. The rag hardstock shows a tendency to remove only very small amounts of alkali. This sample of rag-stock was suitable for high grade bond, banknote and ledger papers. The order in which these various pulps are aligned in their behavior toward dilute alkali solutions

is rather interesting. The ability of pulp fibers to remove alkali appears to be determined, to a very great extent, by the chemical characteristics of the fibers, apparently, the higher the quality of the pulp, the lower the tendency will be to reduce the alkalinity of sodium hydroxide solutions.

THE DETERMINATION OF ALKALI REMOVAL BY CONDUCTIVITY METHODS- In the previously described experiments the loss in alkalinity was determined by the method of direct titration. To obtain further information concerning this action of cellulose fibers on dilute alkali solutions, a few measurements were made on the electrical conductivity of sodium hydroxide solutions before and after being in contact with pulp fibers for a definite period of time. An ordinary, Arrhenius type cell was used, in conjunction with a small potentiometer used as a Wheatstone bridge. The conductivity values were determined at exactly 25 deg. C. The shredded pulp fibers were allowed to stand in contact with the alkali solutions at 20 deg. C. for a period of 30 hours, at a consistence of 4 percent. The fibers were then removed by filtration and the conductivities of the filtrates were determined. Measurements were also made on portions of the untreated solutions, and on distilled water that had been in contact with the pulp fibers under similar conditions. The results are as follows:

Unbleached Sulphite Pulp-

Original Normality	Specific Conductance		After Treatment Corrected
	Before Treatment	After Treatment	
.00141	.000330	.000176	.000056
.00364	.000895	.000355	.000235
.00548	.00135	.000550	.000430
.00756	.00184	.000825	.000705
.00944	.00228	.00117	.00105

The distilled water used in this experiment had a conductivity of .000001 mho, and after being in contact with the pulp fibers the conductivity increased to .000120. The conductivity of the distilled water shows a considerable increase after being in contact with the pulp fibers. It is quite difficult to correct for this disturbing factor, but as a rough approximation, the measured values of the conductances of the filtrates were corrected by deducting the value of the conductance of the white water. These corrected values are given in the last column in the above table. The conductance values are plotted against the original alkali concentration in Fig. 13. The solid-line curves show the actual measurements for the blank solutions and the filtrates. The broken-line curve gives the corrected values for the filtrates. The conductivity of the solutions is appreciably lowered by the contact with the pulp fibers. In Fig. 14, the percent lowering of the conductivity is plotted against the original sodium hydroxide concentration. The reduction in the electrical conductivity should be an index of the removal of the alkalinity. The percent loss in alkalinity for these same solutions, determined by titration methods, is also given in this figure for comparison. The curves differ by about ten percent in actual values, but both curves indicate the pronounced activity of the pulp fibers on these solutions. The value of the conductivity method for determining the loss in alkalinity is limited by the correction that must be applied for the materials that are dissolved from the pulp by the solutions. The solubility of the materials in the pulp fibers will undoubtedly vary somewhat with the concentration of the alkali solutions. However, the results obtained by the conductivity method are in fair agreement with the data obtained by direct titration.

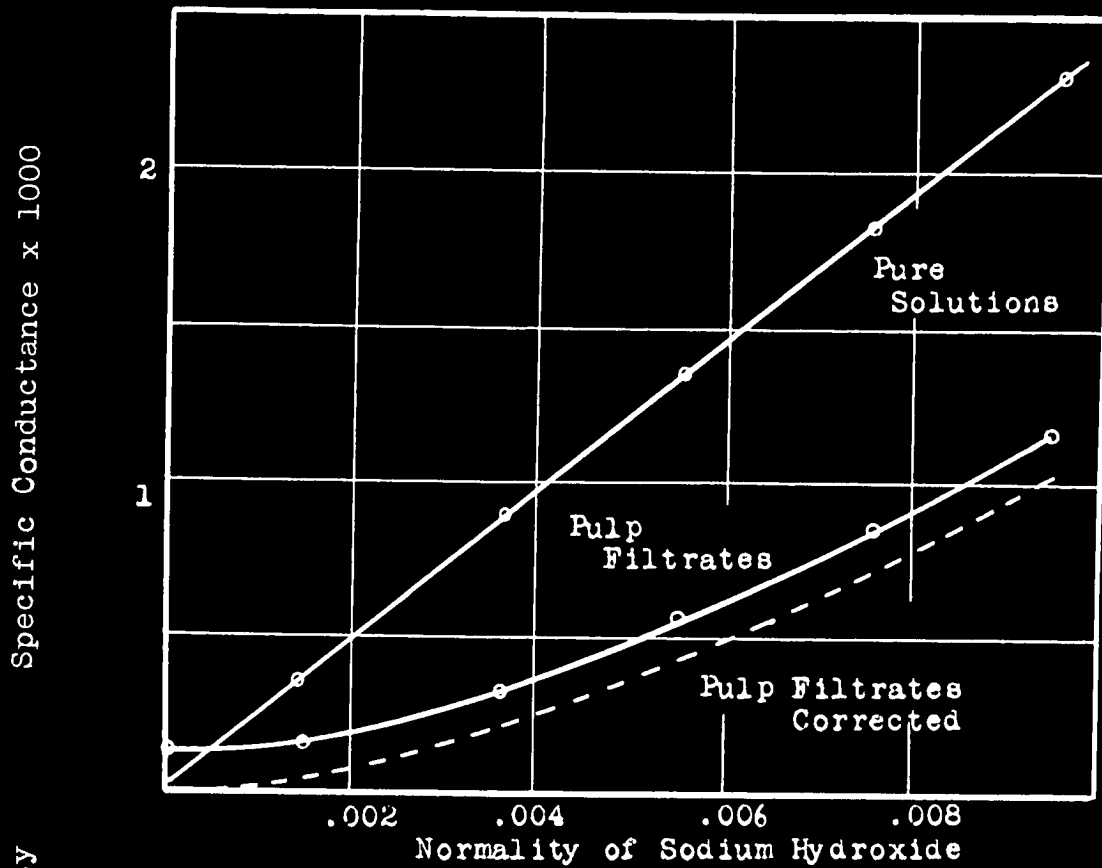


Fig.13. Specific Conductivity of NaOH Solutions before and after Contact with Pulp Fibers

Percent Loss in Alkalinity and Conductivity

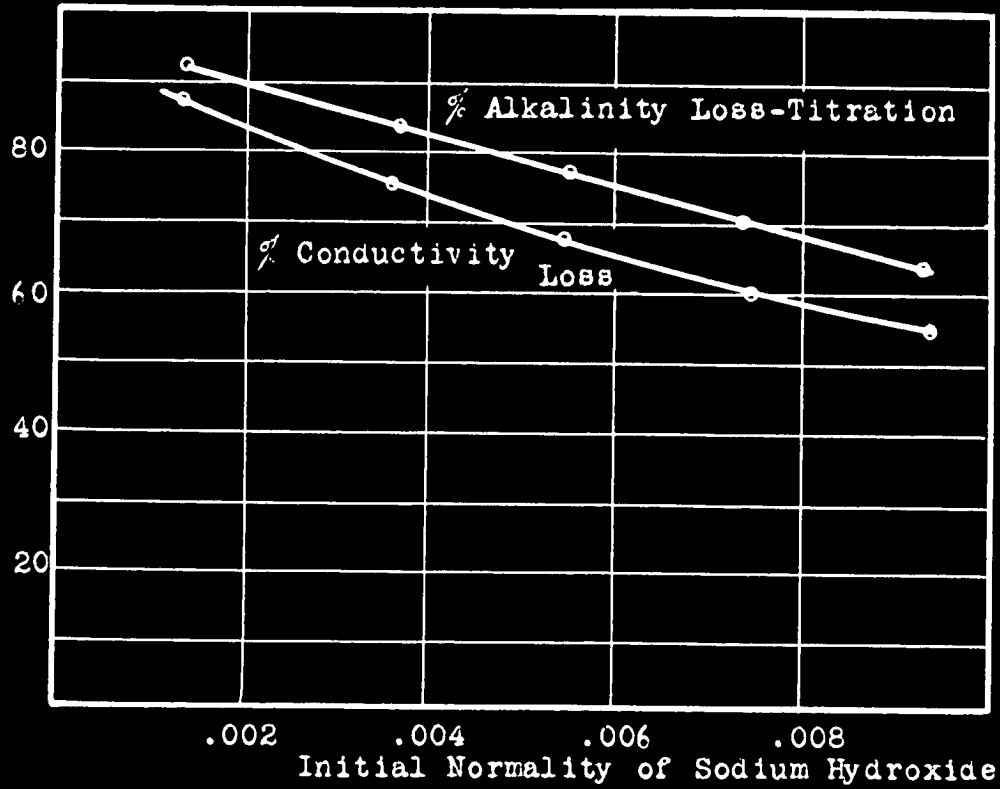


Fig.14. Lowering of Alkalinity and Electrical Conductivity of Sodium Hydroxide Solutions by Pulp Fibers.

If dilute aluminum sulphate solutions are used in place of the alkali solutions the behavior is quite different. The specific conductivity of the filtrates is much higher than the values of the pure solutions. The aluminum sulphate is hydrolyzed in these dilute concentrations, and the alumina is adsorbed by the fibers with the liberation of free sulphuric acid. This liberated sulphuric acid is responsible for the high conductivities of the pulp filtrates in the case of aluminum sulphate solutions.

THE LOWERING OF THE HYDROXYL ION CONCENTRATION OF DILUTE SODIUM HYDROXIDE SOLUTIONS BY COMMERCIAL PULPS.- The determination of alkali by titration methods involving phenolphthalein as indicator gives the total alkalinity above pH-8. The previously described measurements on alkali removal represent changes in the total alkalinity of the solutions, rather than actual changes in the hydroxyl ion concentration. A few determinations were made on the changes in hydroxyl ion concentration due to the presence of pulp fibers, by the method based on the rate of the catalytic decomposition of nitrosotriacetoneamine. In this method it was found that the measurements could be made in the presence of the pulp fibers.

In these experiments, one gram of shredded pulp was placed in the reaction vessel, and 50 cc. of the standard alkali solution were added. The mixture was allowed to stand in the thermostat at 50 deg. C for a period of twenty-four hours with intermittent shaking. At the end of this period, twenty-five cc. of an aqueous solution of the amine were added, and the rate of the decomposition

was determined. The hydroxyl ion concentration was calculated from the reaction constant and the hydroxyl ion constant for this temperature. The concentration of the blank solutions were also determined by this method. The following data show the effect of various commercial pulps on the hydroxyl ion concentration of dilute sodium hydroxide solutions:

THE LOWERING OF THE HYDROXYL ION CONCENTRATION BY COMMERCIAL PULPS

consistence - 2%

Temperature - 50 deg. C.

BLEACHED SULPHITE PULP

Original OH Normality	Final $\overline{\text{OH}}$ Normality	Percent loss in OH ion
.01125	.0094	17
.0090	.0072	19.5
.0056	.0043	26
.0023	.00126	45

BLEACHED MITSCHERLICH SULPHITE

.0113	.0059	48
.0090	.0041	54
.0056	.00185	67
.0023	.00014	94

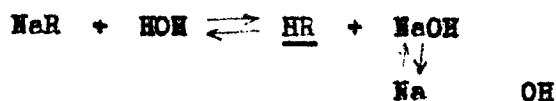
The changes in the hydroxyl ion concentration are similar to the changes in the total alkalinity, but the magnitude of the former are somewhat greater, especially in the more dilute concentrations. These data also show the varied action of different kinds of pulp fibers. The bleached sulphite pulp used in these determinations was of very high quality. Its characteristics approach those of a purified wood fiber or alpha pulp. The activity of this pulp to reduce the hydroxyl ion concentration of the solution is less than half of that of the Mitscherlich sulphite.

All of the previous measurements illustrate the tendency of pulp fibers to reduce the alkalinity of alkali solutions, and also the great difference in behavior of the various pulps. A similar action of the pulp fibers probably occurs in dilute sizing solutions.

THE EFFECT OF COMMERCIAL PULP FIBERS ON DILUTE SODIUM RESINATE SOLUTIONS-

In general mill practice, it is customary to add the size to the beater after the stock and filler have been added, but usually before the alum. In some operations the size is added after a portion or all of the alum has been furnished to the beater, but this procedure is rather exceptional. The rosin is usually added quite early in the beating operation, and the alum is introduced shortly before the beater is to be dumped. The time of contact of the size with the stock depends on the time of beating, this may vary from a small fraction of an hour to several hours. There is usually a period of time in the beating operation in which the stock is in suspension in a dilute rosin soap solution, before the alum is added to precipitate the rosin.

In the dilute concentrations of the beater, the course of the hydrolysis of sodium abietate, probably follows the following equation:



The solubility of abietic acid in water is extremely low, so that any abietic acid that is formed is in a colloidal condition. The sodium hydroxide that is formed, will be completely dissociated at these concentrations. According to the law of mass action, the

above reaction is governed by the following relation:

$$k = \frac{(NaR) (HOH)}{(HR) (NaOH)}$$

where k is a constant depending upon the temperature, and the quantities in the brackets represent the molecular concentrations of the reactants. Since the abietic acid is very insoluble, the value (HR) will be maintained very nearly constant by the colloidal resin, and at these concentrations the value (HOH) is practically constant, the equilibrium conditions may be expressed by the relation-

$$k' = \frac{(NaR)}{(NaOH)}$$

The concentration of the soap is maintained by the alkalinity of the solution. Any condition, which would reduce the sodium hydroxide concentration, would also reduce the concentration of the soap.

The natural hydrolysis of sodium abietate was found to be less than five percent in an N/300 solution at normal temperatures. The concentration of the sizing in the beater, assuming a neutral size, would probably fall in the range between N/1000 and N/100. In beater concentrations, therefore, the extent of the natural hydrolysis of the rosin soap is only several percent, and a large percentage of sodium resinate may be present providing a normal alkalinity of the soap is not reduced. In the beater, however, the normal behavior of the size will be affected by the condition of the water and of the stock. Any materials in the water which will affect the normal alkalinity of the size, will also force the hydrolysis of the soap.

The action of pulp fibers on the alkalinity of dilute sodium hydroxide solutions was discussed in the previous pages. It was found that the alkalinity was greatly reduced by the presence of the pulp fibers, and that the lowering of the alkalinity was determined by the nature of the pulp fibers, other conditions remaining constant. Also, the percentage lowering of the alkalinity increases with greater dilution of the alkali solutions. The percent removal of the available alkalinity by pulp fibers appears to approach 100 percent at infinite dilution. The action of the pulp fibers on dilute alkali solutions should tend to alter the normal equilibrium conditions of the dilute sodium resinate solutions. In dilute sizing solutions the alkalinity is rather low, and the presence of the pulp fibers should produce a great reduction in the free alkali concentration, with a corresponding drop in the concentration of the soap. Under similar conditions, the action of different pulp fibers will probably vary, since the activity of pulp fibers toward alkali removal is quite variable. A study was made on the action of various commercial pulp fibers on dilute sodium resinate solutions. The same series of commercial pulp fibers was used in this study, as was used in the work on the removal of the alkalinity in dilute sodium hydroxide solutions. These pulps show a wide range of behavior toward dilute alkali solutions, and one would expect that the action of these pulps toward sodium resinate solutions would be in the same order as in the case of the sodium hydroxide solutions.

The procedure for making the measurements on the action of pulp fibers on rosin soap solutions was briefly as follows:

Ten gram samples of the shredded pulp fibers were shaken with 250 cc. portions of standard sodium resinate solutions of concentrations ranging between N/500 and N/100. This gave a consistency of pulp fibers in the mixture of 4 percent. The samples were allowed to stand in a thermostat at 25 deg. C. for a period of twenty-four hours. The fibers were then removed by filtering through a bare Buechner funnel, and the filtrates were poured through the mats a second time to obtain a clear solution. The fibers were sucked as dry as possible, and then dried in an oven at 105 deg. C. The fiber mats were then extracted with ether in Soxhlet extractors for four hours. The ether extracts were evaporated to dryness, dried at 105 deg. C. for a period of an hour and then weighed. In a few cases, the soap concentration of the filtrates were determined by precipitating the rosin from an aliquot portion of the filtrate with mineral acid and extracting with ether, and finally weighing the extract. This latter method was found to agree quite closely with the method of extraction of the fibers. The ether solubilities of the untreated fibers were also determined to correct for soluble materials originally present in the fibers. All of the determinations were made in duplicate. The results of these determinations are as follows:

Unbleached Sulphite Pulp:

Original Normality of Sodium Resinate	% HR present based on pulp	% Ether Extract	% Ether Extract (Corrected)
.00278 N	2.1	1.59	0.85
.00556	4.2	2.65	1.91
.00835	6.3	3.63	2.89
.0111	8.4	4.60	3.86
Blank Pulp	---	.74	----

Purified Wood Fiber - Alpha Pulp

.00278	2.1	.418	.36
.00556	4.2	.790	.73
.00835	6.3	1.08	1.02
.0111	8.4	1.33	1.27
Blank Pulp	---	.06	----

Bleached Mitscherlich Sulphite-

Original Normality of Sodium Resinate	% HR present based on pulp	% Ether Extract	% Ether Extract (Corrected)
.00278 M	2.1	.946	.646
.00556	4.2	1.43	1.13
.00835	6.3	1.76	1.46
.0111	8.4	2.00	1.70
Blank Pulp	---	.30	----

Bleached Sulphite Pulp-

.00278	2.1	.78	.48
.00556	4.2	1.25	.95
.00835	6.3	1.60	1.30
.0111	8.4	1.81	1.51
Blank Pulp	---	.30	----

Unbleached Sulphate- Kraft

.00278	2.1	.77	.69
.00556	4.2	1.38	1.30
.00835	6.3	2.02	2.12
.0111	8.4	2.90	2.82
Blank Pulp	---	.08	----

Cotton Cellulose - Rag Hardstock

.00278	2.1	.74	.63
.00556	4.2	.90	.79
.00835	6.3	1.07	.96
.0111	8.4	1.16	1.05
Blank Pulp	---	.11	----

In the above tables, the first column gives the original normality of the sodium resinate in the solutions, the second column shows the amount of abietic acid present in the mixture as the sodium

salt calculated in percent based on the dry fiber. The third column gives the percent ether solubility of the pulp mats, based on the dry fiber, together with the ether solubility of the untreated fiber. The last column shows the percent ether solubility corrected for the materials naturally occurring in the pulp. The six pulps used in this study were the same as those used in the study on the removal of alkalinity of the sodium hydroxide solutions. The above data are represented graphically in Figure 10. In this figure, the percent rosin removed by the pulp (the corrected ether extract) is plotted against the percent rosin originally present in the solution, both percentages are based on the dry weight of the fiber.

The order of the activity of the various pulps toward the sodium resinate solutions appears to be related to the behavior of the pulp fibers toward sodium hydroxide solutions. The rosin determinations were made by the use of ether as a solvent, so that the major portion of the extracts were free rosin or abietic acid. The mechanism by the pulp fibers is probably quite complex. The abietic acid must first be liberated from the sodium salt by the natural or forced hydrolysis, due to the reduction in the normal alkalinity. This free rosin, as it is initially formed, is in a very fine colloidal condition, and could probably be adsorbed or mechanically held by the pulp fibers. Apparently, the retention of this rosin depends on the nature of the pulp fibers. In this connection, a comparison of the curves in Fig. 10. with those of Fig. 9 is of interest. In both cases, all of the wood pulps fall in the same order. The unbleached sulphite pulp, which shows the

greatest activity toward alkali removal, also has the greatest effect on the sodium resinate. The purified wood fiber or alpha pulp exhibits the lowest activity toward both alkali and rosin soap solutions. The remaining wood pulps lie intermediate between the unbleached sulphite pulp and the alpha pulp. However, the removal of rosin by the pulp is not exactly proportional to the ability of the pulp fibers to lower the alkalinity of sodium hydroxide solutions. In their effect on sodium hydroxide solutions, the kraft and the bleached Mitscherlich sulphite pulps are fairly close together, but in the case of the size solutions greater difference appear. The bleached sulphite pulps are grouped closely together in their effect on the rosin soap solutions. The rag-hardstock shows a more or less abnormal behavior toward the rosin soap solutions. It removes a comparatively large amount of rosin from the more dilute soap solutions, but the relative amount removed falls off quite rapidly with increasing concentration of the soap. The ability of a pulp to remove rosin from dilute sodium resinate solutions appears to be determined, to a certain extent, by the capacity of the pulp to lower the alkalinity of the solution. The lowering of the alkalinity of sodium hydroxide solutions by pulp fibers is probably due to several factors, and probably only some of these factors are responsible in forcing the hydrolysis of the soap solutions. The action of different pulp fibers on sizing solutions is quite variable, depending on the nature of the pulp.

The action of a few other pulps on dilute sodium resinate solutions was investigated. A mechanical-pulp made from spruce, an unbleached sulphite made from Western Hemlock, and a high grade

bleached sulphite pulp made from spruce, were selected. The experimental procedure was the same as in the previous work on the effect of pulp fibers on rosin soap solutions.

Mechanical Pulp-Ground wood

Original Normality of Sodium Resinate	% HR present based on pulp	% Ether Extract	% Ether Extract (Corrected)
.00278 M	2.1	1.79	1.35
.00556	4.2	2.25	1.81
.00835	6.3	2.96	2.52
.0111	8.4	3.44	3.00
Blank Pulp	---	0.44	----

Unbleached Sulphite - Hemlock

.00278	2.1	0.76	.47
.00556	4.2	1.44	1.15
.00835	6.3	2.07	1.78
.0111	8.4	2.56	2.27
Blank Pulp	---	.29	2.27

Bleached Sulphite - Spruce

.00278	2.1	0.55	.42
.00556	4.2	1.07	.94
.00835	6.3	1.46	1.33
.0111	8.3	1.55	1.42
Blank Pulp	---	.13	----

These data are plotted in Fig. 11. The ground wood pulp exhibits a rather abnormal behavior, a relatively large amount of rosin is removed in the more dilute solutions, and then the slope of the curve becomes nearly constant. Ground-wood pulp is highly lignified, and a behavior different from chemical pulps would be expected. The unbleached sulphite pulp from Hemlock was an easy bleaching pulp of good quality. The bleached sulphite pulp made from spruce was a special select pulp, suitable for high grade writing papers.

Summary

Measurements were made on the degree of hydrolysis of dilute sodium resinate solutions at concentrations that would be prevalent in the beater. The degree of hydrolysis was determined by the method employed by McBain for generally measuring the hydroxyl ion concentration of soap solutions. This method is based on the rate of the catalytic decomposition of nitrosotriacetoneamine by hydroxyl ions. The degree of hydrolysis of an N/100 sodium abietate solution was found to be 0.54 percent at 30 deg. C. At 56 deg. C. the extent of hydrolysis in an N/300 sodium abietate solution was found to be 4.3 percent. These results are in close agreement with the data reported by Beedle and Bolam (J. Soc. Chem. Ind. 40; 4, 27T, 1921). At 90 deg. C. these authors found the extent of the hydrolysis of .024 N and .012 N sodium abietate solutions to be 4.0 and 5.7 percent respectively. The determination of the degree of hydrolysis of soap solutions by the method based on the catalytic decomposition of nitrosotriacetoneamine, was shown by McBain to be in excellent agreement with the hydrolysis determination based on the method involving electromotive force measurements. The above data on the hydrolysis of neutral sodium resinate solutions are contrary to the results of Ivanoff (Bumazhnaia Promyshlenost, 1; 33, 1922). Ivanoff found that at a dilution of 0.5 gram of rosin per liter (0.0015 N sodium resinate) as much as 95 percent of the rosin is free. An 0.0015 N sodium resinate solution shows a slight turbidity, but the turbidity can hardly be due to 95 percent of

the rosin present, since on the addition of a mineral acid a very much greater turbidity is produced. Measurements were also made on the electrical conductivity of sodium resinate solutions. The increase in the equivalent conductance between the concentrations of $N/100$ and $N/1000$ is not very great, showing that no great changes are taking place in the constitution of the electrolyte in this concentration range. The equivalent conductance of the sodium resinate solutions are high, but there does not appear to be any pronounced tendency of the conductance curve toward approaching the conductance curve of sodium hydroxide, which would be a rough indication of hydrolytic effects. At the concentrations prevailing in the beater, the extent of the hydrolysis of sodium resinate or neutral size is only several percent, and a major portion of the neutral size can exist in solution as sodium resinate. The stability of the rosin soap in the beater is determined mainly by the alkalinity of the beater water.

It was found that commercial pulp fibers have a great tendency to lower the alkalinity of dilute sodium hydroxide solutions. In the concentration range between $N/1000$ and $N/100$, the alkali removal curves by the pulp fibers resemble typical adsorption curves, but the mechanism of the alkali removal can not be due to true adsorption processes, since higher temperatures favor a great alkali removal. The time necessary for equilibrium conditions to be established between the solutions and the pulp fibers is rather long. A great reduction in alkalinity of the solutions occurs in the initial hours of contact with the pulp fibers; the reduction in alkalinity becomes nearly constant in

the moreconcentrated solutions after seventy hours, but a slight, increase in alkali removal is still noticable after this period of time, especially in the more dilute solutions (see Fig. 5). The lowering of the alkalinity is very appreciable for most commercial pulps in an N/500 sodium hydroxide solution, several pulps remove 80 - 90 percent of the available alkalinity. The activity of a pulp to remove alkali appears to be determined by the nature of the pulp; the behavior of different pulp fibers is quite variable. Unbleached pulps exhibit a great activity toward alkali removal, bleached chemical pulps have an intermediate effect, and purified wood fiber and rag-stock show the lowest activities. (Fig. 9).

The lowering of the alkalinity of dilute sodium hydroxide solutions by pulp fibers was determined by titration methods. Additional measurements were made on the reduction in the electrical conductivity of sodium hydroxide solutions due to presence of pulp fibers. Measurements were also made on the reduction of the hydroxyl ion concentration of sodium hydroxide solutions due to the presence of pulp fibers, by a method based on the rate of the catalytic decomposition of nitrosotriacetoneamine by hydroxyl ions. All of these measurements indicate the great activity of pulp fibers toward reducing the alkalinity of dilute sodium hydroxide solutions, and the great differences in behavior of the various pulps.

The activity of pulp fibers toward lowering the alkalinity of dilute alkali solutions should have an effect on the normal hydrolysis of neutral size solutions. The stability of sodium resinate solutions is determined by the natural alkalinity of these

solutions. If this alkalinity is removed, hydrolysis will take place to restore the equilibrium, with the liberation of free abietic acid. Since different pulps have a varied action in this respect the amount of abietic acid liberated, will vary with the kind of pulp. The behavior of commercial pulps toward dilute sodium resinate solutions was studied, and the results indicate that the various pulps have a variable action on these solutions. The amount of rosin liberated from the solutions and retained by the pulp fibers is dependent on the nature of the pulp. Pulp fibers which retain a relatively large amount of rosin, also show a great tendency toward lowering the alkalinity of sodium hydroxide solutions. For a series of different pulps, the activity toward alkali removal is not exactly proportional to the effect of these pulps on the soap solutions, but nevertheless, the action of the pulp fibers on the rosin solutions appears to be closely related to the activity of the pulp fibers toward alkali removal (Fig. 9 and 10). These experiments seem to indicate that the presence of the pulp fibers forces the hydrolysis of the sodium resinate. Since no other agent was used in these experiments to precipitate the rosin, the amount of rosin retained by the fibers was determined primarily by the following factors: First, the amount of free rosin liberated from the soap solution by the action of the pulp fibers on the alkalinity of the solution and second, the ability of the pulp fibers to retain this liberated rosin. There is the possibility of the pulp fibers removing the rosin from the solution as sodium resinate, and probably a portion of the rosin found in the fibers was present as the sodium salt, but due to the effect of the pulp fibers on the alkalinity of the soap solutions, it is

quite likely that the rosin found in the fibers is primarily the liberated, colloidal abietic acid.

In commercial practice, experience has shown, that in general, the higher the cellulosic purity of the stock, the more difficult it is to produce efficient sizing with rosin. It has been found that rag stock and alpha fiber are more difficult to size than bleached sulphite, the bleached sulphite pulp in turn, presents greater sizing difficulties than an unbleached fiber. This behavior of the various commercial pulps resembles the activity of these pulps toward dilute sodium hydroxide and resinate solutions. The nature of the pulp fibers appears to be a rather important factor in the problem of rosin sizing.

Conclusions

From the results obtained in this investigation we may draw the following conclusions:

1. The natural hydrolysis of sodium resinate solutions is not very great at beater concentration. The extent of hydrolysis of an N/100 sodium abietate solution was found to be 0.50 percent, at 30 deg. C. For an N/300 sodium abietate solution at 56 deg. C, the extent of hydrolysis was found to be 4.3 percent. In the case of a neutral size, a large portion of the size can exist in the beater as sodium resinate, providing there are no factors which will affect the hydrolytic alkalinity of the solution.
2. Pulp fibers show a tendency to lower the alkalinity of very dilute sodium hydroxide solutions. The activity of the various commercial pulps in this connection, appears to be determined by the nature of the pulp, its method of preparation, impurities, etc. In general, the higher the cellulose purity of the pulp, the lower the activity of the pulp toward dilute alkaline solutions.
3. Due to the tendency of pulp fibers to lower the alkalinity of dilute alkaline solutions, pulp fibers will tend to force the hydrolysis of dilute sodium resinate solutions. The extent to which the hydrolysis of the rosin size is forced, by the pulp fibers, appears to be closely related to the activity of the pulp fibers toward lowering the alkalinity of dilute alkaline solutions.