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The Retention of Wet Strength Resins as Determined by the Kjeldahl Method

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Thesis 436A

THE RETENTION OF WET STRENGTH RESINS AS
DETERMINED BY THE KJELDAHL METHOD

Submitted by
Walter J. Redmond

INDEX

	Page
General properties of various wet strength resins . . .	1
Mechanism of retention of wet strength resins . . .	9
Factors affecting the retention of wet strength resins .	15
Effect of anions	15
Effect of cations	19
Effect of pH	20
Type of fiber	22
Cooking and bleaching residues	22
Kjeldahl nitrogen determination of wet strength resins .	23
Apparatus	24
Reagents	24
Procedure	25
Report	27
Literature cited	28

GENERAL PROPERTIES OF VARIOUS WET STRENGTH RESINS

True wet strength is not a ~~grade~~ of water proofness of paper, but is a measure of the residual strength of the paper gauged by the mullen, tear, burst, and fold, after the paper has been completely soaked in water and the resistance to water penetration has been completely broken (1).

To increase the wet-strength of paper, a number of different resins may be applied, and these resins may be broadly classified as anionic or cationic in nature. Of these resins, three particular resins will be discussed, cationic melamine-formaldehyde, anionic urea-formaldehyde, and cationic urea-formaldehyde.

It is the purpose of this article to discuss the retention of the above named resins, but before discussing the mechanisms of retention and factors affecting the retention of these resins, it may be well to have a ~~partial~~ understanding of these resins.

In the application of resins to stock, the particles of the resins are colloidal in nature and are deposited on the paper stock by an electrostatic force (2). Melamine-formaldehyde and modified urea-formaldehyde are cationic in nature and have a direct affinity for the anionic paper fibers. Unmodified urea-formaldehyde is anionic in nature and requires the use of a mordanting agent such as alum to obtain efficient absorption of the colloidal resin particles on the surface of the fibers.

^{10' mine}
Melamine-formaldehyde resin is formed by the addition of formaldehyde to the ~~me~~ melamine ring. Melamine is a nitrogenous organic

compound. It is basically a triazine consisting of a six membered ring with alternating carbon and nitrogen atoms. Attached to each of the three carbons are three amino groups, one group for each carbon (1). It is to these amino groups that the formaldehyde are attached. Since each amino group contains two hydrogens, and there are three amino groups in a melamine molecule, melamine has a functionality of six. Of these six possible derivatives only trimethylol and hexamethylol melamine have been isolated (15). However, for wet-strengthening of papers, it is necessary to keep the ratio of melamine and formaldehyde in a range that will produce either a soluble or easily dispersible product. This ratio may vary from 1:1 to 1:0.8.

The resulting resin is dissolved in water and hydrochloric acid to form a cationic, water-dilutable, colloidal resin. For best results, the resin is dissolved at ten to fifteen percent solids along with hydrochloric acid in the proportions of from 0.6 to 0.8 moles of acid to 1 mole of melamine resin. The colloid thus formed is characterized by a bluish haze (1,15).

Melamine resins are extremely ^{sensitive} sensible to acids, even when acids used are only in slight traces. These acids rapidly catalyze the resin to form gels. However, due to the slight basicity and salt forming properties of the resin, the formation of gels may be avoided (5). If a strong acid is added to the soluble melamine-formaldehyde resin, something akin to salt formation takes place and the resulting polycondensate molecule becomes cationic in nature.

Due to the functionality of the melamine molecule, it necessary to prevent cross linking between the molecules. This is possible at low ^{va}temperatures and at high dilutions. Under these conditions, the molecules are capable of forming larger linear molecules, without gelation or precipitation (5). The following aging period then results in the formation of highly condensed cationic water dispersable resin molecules which are well suited for absorption onto anionic pulp fibers.

It is of special ^eintrest to note that the acid used to convert the resin into a cationic colloidal suspension is not retained by the paper stock when the sheet is formed, but is removed with the white water (14). The acid used therefore does not have a detrimental effect on the paper. The resin is cured on the paper machine by the usual drying ^{va}temperatures of 250°- 300° F, where the linear molecules of the resin take two and three dimensional shapes.

General properties of urea-formaldehyde resins. Urea-formaldehyde

resins have a great variety of uses in enamels, adhesives, molded and laminated products, treatment of textiles, and the improvement of the physical properties of papers. Of special ^eintrest to the paper industry are the water soluble types of urea-formaldehyde. In the class of water-soluble resins, the various properties and performances can be varied greatly. Permutation of such variables as the degree of condensation, urea-formaldehyde ratio, nature of correagent, and amount of correagent give a number of possibilities to design a urea-formaldehyde resin to fit almost any ap-

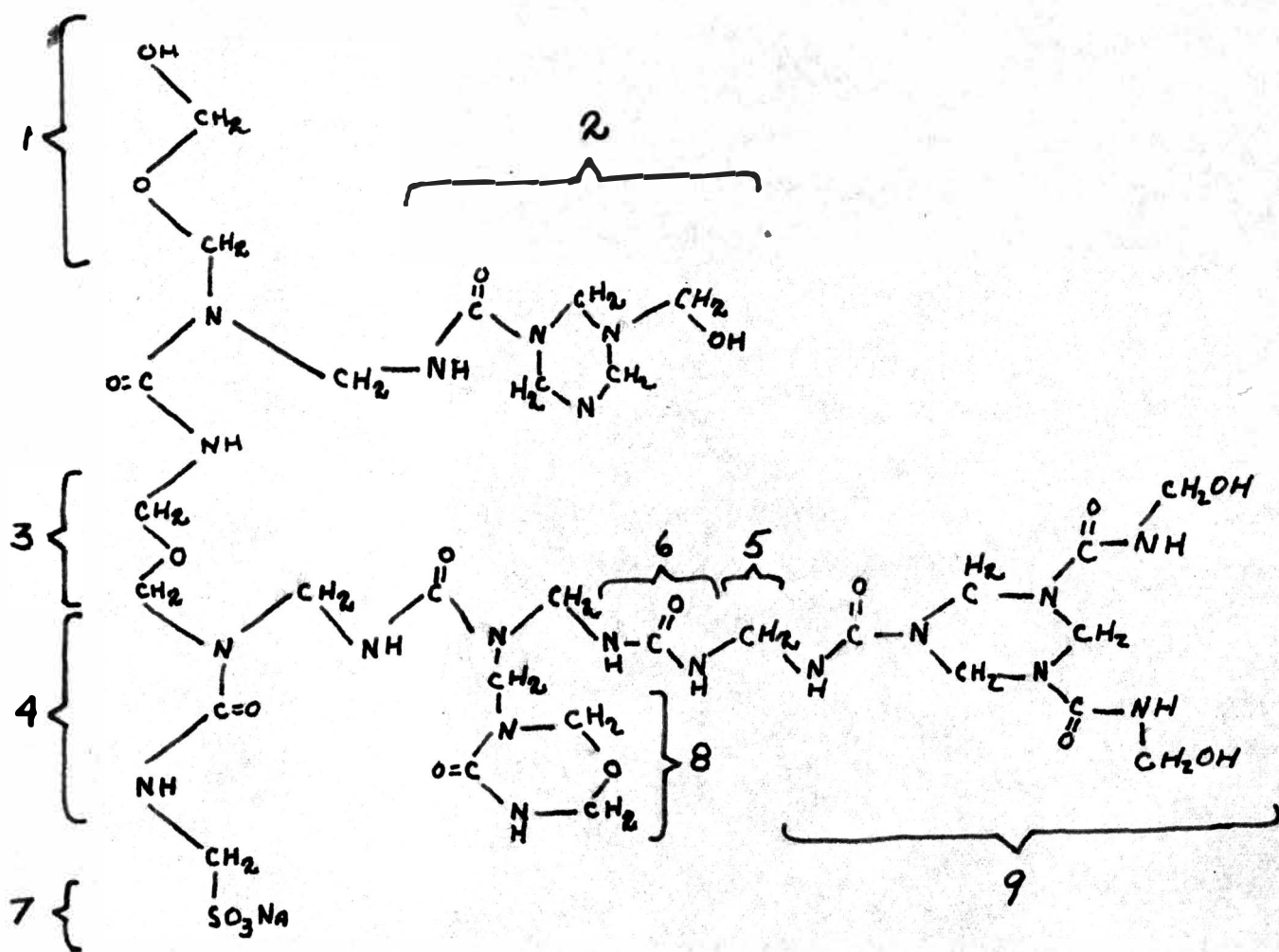
plication (3).

Table II shows an example of a possible structural formula for a commercial correacted urea-formaldehyde resin (Uformite 467) which shows some of the possible variations of the resin (3).

Of the most obvious of the grosser features of the resin which are subject to control is the molecular size or the degree of condensation. Slightly condensed preparations can be made with a molecular weight of 100. This resin gives a water thin aqueous solution and can easily be distributed uniformly over the surface of the fibers. Highly condensed preparations can have undeterminedly high molecular weights. These resins give aqueous solutions which are quite viscous and may be completely non-diffusable in cellulose. When applied to paper, these resins can only remain on the surface of the fibers.

The degree of condensation of the urea-formaldehyde resins also have an effect on the behavior of the resin when in solution. The highly condensed resins give colloidal suspensions which show the Tyndall effect (3). The stability of the solution is sensitive to the degree of condensation on the addition of pulp, salts, or other solutes.

Another obvious variable is the extent of branching in the polymolecular chain. The extent of branching in any chain depends on the degree of condensation of the molecules and on the urea-formaldehyde ratio. If the ratio is equal to one, only linear molecules may be formed. When the ratio is equal to two, a branch may occur at every urea unit (3). Solubility and colloidal properties may be expected to respond to changes in the branching of the resin.



- (1) Hydroxymethoxymethyl group
 (2) Triazone ring (dimer)
 (3) Dimethelene ether linkage
 (4) Trifunctional urea
 (5) Methelene bridge linkage

- (6) Difunctional urea
 (7) Anionic bisulfite solubilizing group
 (8) Uron ring
 (9) Triazine ring (trimeric)

TABLE ~~II~~ I

Possible Variations of Correacted Urea-Formaldehyde Resin

The solubility of the resin is also affected by the methylol groups present, which is one combined form of formaldehyde, which contributes hydrophilic properties to the resin. This fact further explains the extreme sensitivity of the solution and colloidal properties of the resin to variations of the urea-formaldehyde ratio.

The great ^aversatility of the urea-formaldehyde resin is enhanced by the possibility of reacting other reagents into the polymer molecule. In the example on table ^I11, sodium bisulphite is used as a correagent. Sodium bisulphite is extremely hydrophilic and permits the resin to be water soluble at higher degrees of condensation and at lower formaldehyde ratios than would otherwise be possible.(3). Bisulphite is only one of the large number of reagents that may be incorporated into the urea-formaldehyde molecule.

The type of urea-formaldehyde that is made soluble by correagenting with sodium bisulfite results in a resin that is anionic in nature. Another type of modified urea-formaldehyde may be produced by reacting with the initial water soluble condensation products of urea and formaldehyde certain polyhydric phenols.(13). These modified resins are so chemically modified that they exhibit satisfactory disperseability in aqueous solutions with excellent substantive or adhesive effects for cellulose fibers.

The modification of urea-formaldehyde resins by the use of certain polyhydric phenols yields condensation products that are soluble in alk^aaline solutions including very dilute ^aalkaline solutions., but they are partially to completely insoluble in neutral or acidified solutions. In acidified water, modified or polyhydric

correacted resins produce colloidal dispersions that are cationic in nature and which are deposited on the cellulose fibers in less time than the unmodified resins (13).

The polyhydric phenols which have been found useful in the modification of urea-formaldehyde are those having at least two hydroxyl groups in meta position to each other (13). They must also have at least one individual hydrogen in ortho position to each meta hydroxyl group. The specific phenols which may be included in this class are; resorcinol, phloroglucinol, pyrogallol, and many similar phenols.

The exact chemical combination in the reaction between the polyhydric phenols and the wet-strength condensation products is at present not clear (13). However analytical studies show the phenols to be firmly attached to the polycondensate because once reacted, the phenol can neither be detected nor can it be separated.

It has been found (13) that the maximum solubility of the modified resin in an alkaline solution is obtained by correacting a 3-5% quantity of a polyhydric phenol, such a mixture also exhibits excellent dispersability when highly diluted with acidified water.

Mechanism of Retention of

Wet Strength Resins

The ideal wet strength resin may be defined as one which will be one hundred percent retained when added to cellulosic pulp fibers. With melamine formaldehyde resin and certain urea formaldehyde resins, it is possible to obtain one hundred percent retention under favorable conditions. This is thought to be because of the mutual coagulation between the resin and the pulp fibers. However under ordinary operating conditions, no resin meets this requirement, but fall far short, although some resins are better retained than others (17). On the other hand, it may well be said that resin retention itself is not an acceptable basis to compare the values of the different resins, but it is very useful when it is desired to make a study of the various factors affecting the efficiency of the resins.

Since the wet strength resins are colloidal in nature under normal operating conditions and most resins exhibit an electrostatic charge, it follows that the factors influencing the mechanism of retention will be greatly influenced by the pH of the dispersion. It will be assumed in the following discussion that the pH and the rest of the influencing factors will be ideal values and the effects of these factors will be discussed separately at a latter time.

A number of different theories concerning the mechanism of retention of the wet strength resins have been postulated. The attachment of the resin molecules to the surface of the pulp fibers may be due to any one of the postulated theories, or may be due to any number of reasons all of which are purely speculative and there is no apparent basis for choosing any one in particular (8).

First we shall consider the conclusions which were developed from the modern theories of the ionic character of cellulosic fibers. These theories were developed in connection with the application of rosin, dyes, and fillers. It is necessary to consider these theories, because it shows that the problems of retention of wet strength resins are essentially the same as other retention problems(8). The anionic character of the pulp fibers is most easily shown by the fact that basic dyes, which are cationic in nature, are retained by the cellulose fibers, while acid dyes, which are anionic in nature are not retained by the pulp and require the use of mordanting agents for retention (9).

In experiments carried out by Fineman and Gruntfest (8), different pulps were tested with and without alum. A comparison was made between anionic and cationic urea formaldehyde resins and melamine formaldehyde resin.

In the first test, bleached sulphite without alum was considered. In this experiment the implication was that only cationic resins would be retained. The results were found to be entirely compatible with the current theories of the anionic character of wood pulp fibers.

In the second and third experiments, unbleached sulphate and bleached sulphite with 3% alum were used. The purpose of these experiments was to point out the mordanting effect of the alum between the pulp and the anionic wet strength resins. These results also proved to be entirely compatible with the modern theories of the anionic character of the pulp. They also showed that urea resins can give completely different results and that they cannot

be compared as a class unless the characteristics of the resin being considered are first carefully defined.

For the fourth test, unbleached kraft without alum was used. The results were comparable to the bleached sulphite without alum except that the anionic character of the urea resins was less conspicuous indicating that there are factors other than the ionic character of the resin which may be operative, especially when unbleached pulps are used.

Gruntfest points out that the ionic character of the pulp may be due to different functional groups (9). For example, unbleached sulphite contains a substantial amount of sulphonated lignin which exhibits a substantial amount of anionic electrostatic charge, over a wide range of pH values. Bleached sulphite, which contains hardly any sulphonated lignin, is anionic in nature due to the carboxyl groups present in the cellulose, and these groups do not exhibit an electrostatic charge, except over a small pH range.

The attraction that exists between the negatively charged pulp fibers and the cationic resins may be explained by at least three theories, all of which are purely speculative and there is no particular evidence to support any particular one.

The two most popular theories to date were pointed out by Fineman and Reynolds (8,10). One theory suggests that an attraction may exist between the resin nitrogens and the surface of the fibers. Such an attraction may be due to the slight basicity or salt forming properties of the nitrogen, which may form a covalent bond with the pulp fibers. Another possible speculation would sug-

gest the formation of hydrogen bonds between nitrogens of the resins and the hydroxyl groups of the cellulose fibers.

In using melamine formaldehyde resins, the resins are prepared by dissolving the resin in a strong acid other than sulphuric (14), and allowing the solution to age. The resulting solution converts the resin into a cationic colloidal dispersion. These colloids exhibit a fairly strong electrostatic charge and may be absorbed from solutions by cellulosic materials containing an anionic charge. This seems to make the retention of wet strength resins a simple problem and a resin with a cationic character would be the answer. However, the favorable properties that seem to be in favor of the resin can be reversible and hinder the retention of the resin. If a bleached pulp is used, its anionic properties are due to carboxyl groups that are present in the cellulose molecule. If a strongly charged resin colloid such as melamine formaldehyde is added to the bleached pulp, the anionic character of the pulp may become cationic when only a small amount of resin is added. Gruntfest points this out by showing that it is possible to obtain saturation on the surface of the fiber when only 2% resin is added (9).

The problem of the mechanism of retention of urea formaldehyde is more complicated than that of melamine formaldehyde, unless the conditions of the resin are specified. The electrical character of the urea formaldehyde resin can be so tailor made by the organic chemist, that there can be no definite definition of the electrical character of the resin. By controlling the reaction conditions of the resin and by using various correagents, the charge density ^{and} nature can be controlled. By using various correagents, it is possible

to produce urea formaldehyde resins that are strongly cationic, mildly cationic, nonionic, or anionic (9).

In using anionic urea formaldehyde as a wet strength resin, it is necessary to consider a number of properties of the pulp and of the resin which effect the electrostatic charge of the resin. In the first place, it is necessary to use some sort of a mordanting agent such as alum. Secondly it is necessary to consider the amount of electrostatic charge of the pulp (whether the charge is due to carboxyl groups or to sulphonated groups). Thirdly it is necessary to consider the nature of the correagent.

The effect of the mordanting agent offers a problem which is greatly affected by the pH of the solution and is discussed in detail in the effects of pH on the retention of urea formaldehyde resin.

The amount of electrostatic charge is extremely important in the use of urea formaldehyde. The resin is retained by pulps that exhibit a considerable anionic charge, such as that contained by unbleached pulps. However, when the electrostatic charge of the pulps is low and due to the presence of carboxyl groups, the resin shows a considerable decrease in retention (9).

The electrical character of the correagent is what determines the electrical charge of the resin. In the production of anionic urea formaldehyde, sodium bisulphite is used as a correagent. The anionic character of the bisulphite increases the negativity of the resin. When in solution, electrolysis studies show the resin to be ionized and the resin molecule to migrate towards the anode. (3).

The negativity of the resin may also be shown by the addition of cationic colloids to a resin solution. The addition of alum to a resin solution produces a cationic colloid in the pH range above four. In this state, the resin colloid reacts with the alum colloid and they slowly agglomerate to form a precipitate. In the presence of anionic pulp fibers, a three way interaction takes place between the fibers, the resin, and the alum. It is this principle that is responsible for the retention of the resin on the surface of the pulp fibers (3). It should be noted that the amino groups of the resin do not impart much basicity to the resin because of the presence of the C=O group and because of the presence of the cor-reacted bisulphite. (10).

Due to the obvious problems ~~affronted~~^N by the use of anionic urea formaldehyde, much work has been done to reverse the polarity of the resin colloid from anionic to cationic. It was believed that the desired objective could be obtained by incorporating polar basic groups into the resin. It was found that this may be done by cor-reacting such groups as the amino or imino (10), or by correacting certain polyhydric phenols (13) along with the resin.

In the preparation of polyhydric phenol correacted urea formaldehyde, the reaction may be separated into two stages. The first stage is characterized by the loss of solubility in water. This first stage can be dissolved in alkaline solutions, but is not stable and develops cloudiness and precipitates within one hour. The second stage is produced by further reacting beyond the first stage. The second stage is characterized by the formation of a viscous, resinous mass that is soluble in alkaline solutions and is very stable (13).

When the second stage of the resin is mixed with an acidified pulp suspension, the resin slowly precipitates onto the surface of the fibers. When this same second stage resin is first dissolved in an alkaline solution and then mixed with an acidified pulp suspension, the resin is rapidly deposited on the surface of the fiber, and it is usually only a matter of minutes before the resin is completely deposited on the surface of the fibers.

If the charge density of the modified urea resin is not carefully controlled, the same trouble may be encountered as that which occurs when using melamine formaldehyde. That is, if the pulp charge is low and the electrostatic charge of the resin is high, a saturation of the resin on the surface of the fibers may occur when only a small amount of the resin is added. However, if the electrostatic charge of the modified resin is controlled, it is possible to add a considerable quantity of resin without obtaining saturation (9).

FACTORS AFFECTING THE RETENTION OF WET STRENGTH RESINS

Due to the colloidal nature of the various resins, it might be expected that anions, cations, pH values, and many other factors would greatly affect the retention of the various resins. Observations of laboratory research and commercial operations have been ⁰thoroughly investigated as to the factors influencing the efficiency of retention of the various resins and there have been many articles published which ~~thoroughly~~ ^{thoroughly} cover most of the factors in question.

Effect of anions— The effect of anions on the retention of the different resins exhibits a serious problem in the retention of cationic resins, but does not have to much effect on the retention of anionic resins.

Maxwell and Reynolds (4) made a direct comparison of several different valent anions. The pulp was washed with demineralized water and suspended in demineralized water. The pulp was treated with various amounts of mono-valent, divalent, and tri-valent anions before the addition of three percent melamine formaldehyde resin. Three sets of tests were made with varying amounts of alum and the pH of the solution was fixed at 4.5 with HCl or NaOH. The results are tabulated in the following table. Column I represents the resin retained in the sheet when no alum was added. Column II represents the amount of resin retained by the pulp when three percent alum was added to the pulp before the melamine resin. Column III represents the resin retention when the pH of the solution was adjusted at 4.5 by the use of alum before the addition of the resin to the stock. The concentration of the salts was fixed at 1600 ppm.

Salts Added	1	11	111
Demin. water	1.5	2.1	2.2
Tap water	2.3	2.1	2.3
CaCl ₂	2.3	2.2	2.2
MgSO ₄	1.4	1.1	1.3
Na ₂ SO ₄	1.5	1.2	1.2
MgCO ₃	2.2	2.2	1.2
NaH ₂ PO ₄	2.0	---	---

TABLE

The effect of alum on the retention of melamine formaldehyde

The above experiments show that the sulphate ion concentration plays a very important part in the melamine formaldehyde resin retention. As is shown, the effect is sometimes beneficial and at other times, the effect is non-beneficial. It would be expected that other anions would have the same effect as the sulphate ion, but a lesser effect for the lower valent ions at the same concentration as the sulphate ions, and a greater effect for the higher valent ions at the same concentration as the sulphate ion. (4). The reason the carbonate and phosphate ions acted as if they were monovalent is because at a pH of 4.5, they exist as the bicarbonate radical and the dihydrogen phosphate radical.

To show the effect of different valent ions at the same concentration, experiments were made with mono, di, and tri valent ions. The results as depicted in the graph in figure 1, show ~~definitely~~ ^{definitely where} that the valency of the anion play a major role in determining the retention of the melamine resin (4). The curves shown by the graph in figure 1 represent the resin retention as the concentration of all three valent ^{ions} were increased. The effects of the tri valent ions is shown only as a matter of interest and can be neglected because ^{the} ~~are~~ ^{trivalent ions} rarely used. Because of the high concentration of the mono

When? (18)

needed to

too much trouble

valent ions cause any trouble, it could be assumed that they would show no troublesome effects. The biggest trouble in the use of melamine formaldehyde resin is the adverse effect produced by the use of bivalent or sulphate ions, since these ions are the most prevalent in the paper industry. It has been found that the retention of the melamine resin decreases with the valency of the anions in the magnitude of 1:10:30, and optimum retention is obtained when the concentration of the anions is in the magnitude of 750 ppm for mono valent anions, 75 ppm for bivalent anions, and 25 ppm for trivalent anions (6).

To bear out this point, tests were made to find the optimum retention of the resin with alum as the anion. All of the variables were kept constant except for the concentration of the sulphate ion. The sulphate ion concentration was varied from 0-1600 ppm. In half of the sets, three percent resin was added before the alum, and in the other half, the resin was added after the alum. The results depicted by the graph in figure 11, show the resin retention to increase to a certain point as the alum concentration is increased and then to decrease as the concentration of the alum is increased beyond this point, when the resin was added after the alum. When the resin was added before the alum, there was no decrease in the resin retention as the amount of alum added was increased. (4).

The effect of anions on the resin retention could be due to two factors. They could either destroy the surface activity of the fiber, or they could destroy the colloidal properties of the resin. Because it would be impossible to study or to test the reduction in the surface activity of the fibers, Maxwell and Reynolds made tests on the effect of the sulphate ions on the melamin resin in the ab-

ence paper fibers (4).

To study this point, the melamine formaldehyde and hydrochloric acid solution was allowed to age at twelve percent solids for different intervals of time. The concentration of the sulphate ion was also varied. The results showed that the sulphate ion had less effect on the resin as the resin was allowed to age.

Similar tests were made using the same intervals of time for the aging of the resin and the same percentage of solids of the resin. In these tests, sodium chloride was used to furnish the anions. The results obtained were entirely compatible with those obtained when alum was used to furnish the cations, the only difference being that higher concentrations of the sodium chloride were needed to obtain the same results.

In using an~~x~~ionic urea formaldehyde resins, the use of anions does not impair the retention of the resin as in the case of the melamine formaldehyde resin. However, the efficiency of the resin may be impaired when high concentrations of the anions are used. (8).

Certain other modified urea resins which are cationic in nature and therefore strongly attracted to paper fibers, may be so modified and their charge density so adjusted, that the use of anions does not interfere with the interaction of the resin colloid and the pulp fibers (3). Results of tests conducted by Fineman and Gruntfest (7) show that sulphate ions are relatively unimportant in the retention and performance of cationic urea formaldehyde resins.

Effect of cations - Melamine formaldehyde and cationic urea form-

aldehyde resins are not affected by the use of cations (6), But the use of cations is directly responsible for the retention of anionic urea formaldehyde.

Since the urea resin is anionic in nature and the pulp fibers are also anionic by character, a cationic mordanting agent is required to attach the resin to the pulp. When alum is added to the resin, a precipitate is formed as the alum and the resin agglomerate and the resulting colloid is cationic, Due to the aluminum ions. In the presence of anionic pulp fibers, a three way interaction takes place between the resin, alum, and pulp fibers. It is mainly this reaction that is responsible for the retention of the anionic resin (3).

Effect of pH - In considering the effects of pH on the retention of the various resins, it is necessary not only to study the effects on the resin colloids, but also the effect of pH on the pulp fibers and when anionic urea formaldehyde is being used, the effect of pH on the aluminum hydroxide precipitate.

The effect of pH on melamine and urea formaldehyde resins is very much like a salting out effect. When the resins are added to an acid solution, a clouding effect is first noticed. After some time, the resin completely separates from the water solution. It was first thought that this precipitating effect of the acid precipitated the resin onto the surface of the fiber. (16).

On the other hand, it was known that a low pH is essential as a catalyst and that no matter how much the treated paper was cured, no wet strength could be obtained unless a sufficiently low pH is used.

1 In using melamine formaldehyde resin, the normal range of papermaking pH values of 4.5-6.5 is sufficient to produce satisfactory results. At pH values below 4.5, the electrostatic charge of the resin and that of the pulp is greatly diminished and the retention of the resin is also greatly reduced. On the other hand, low pH values favor better wet strength properties and less curing time. At higher pH values, more of the resin is retained by the fibers, but the final wet strength is considerably decreased and the necessary curing time is increased. Experiments have shown that the most satisfactory results are obtained if the pH range is between 4.5-5.5 when using melamine formaldehyde resins.

When using melamine formaldehyde resin in commercial operations, ^{maybe} it is necessary to add a basic salt such as sodium carbonate to offset undesirable drops in pH due to the hydrochloric acid used in solubilizing the resin.

When considering the effect of pH on anionic urea formaldehyde resin, it is also necessary to consider the effect of pH on the cor-reactant and also the effect on the mordanting agent being used.

The urea formaldehyde resin may be made soluble by sulphomethylation of the resin which results in an anionic resin molecule which require the use of a mordanting agent for retention, in most cases the agent used is alum.

The cationic properties of alum are extremely sensitive to pH values above 4 and ^{it} began to lose its properties above this range. Below this range, the aluminum ion exhibits a fairly strong cationic charge. It is also in this range that the carboxyl groups, which contribute to the anionic character of the pulp began to lose their

anionic character^c. Gruntfest (9) points out that the carboxyl groups of bleached pulps are anionic only at higher pH values and began to lose their anionic character^c at pH values near four. When unbleached pulps are used, their anionic character^c is due largely to sulfonated lignin groups which exhibit their anionic charge at either high or low pH values. It follows that when bleached pulps are ~~being~~ used with anionic urea formaldehyde resin, the pH range is small in which the carboxyl groups are sufficiently anionic and the alum is sufficiently cationic to give good resin retention and requires very close attention.

Type of fiber - All paper making cellulose fibers may be used with all three types of resins, and the retention of the resins is not seriously affected by the different types of fibers (6,3), although the capacity for taking wet strength may vary slightly according to ~~the location~~ ^{the} origin of the fibers. However, the difference is so small that this factor is overshadowed by the other factors.

Cooking and bleaching residues - Most mills operate with pulp that is relatively free from cooking and bleaching residues, but it is necessary to consider this point because it is very possible that conditions do exist where these residues are left in the pulp.

Results of experiments on the effects of bleaching residues showed ~~definitely~~ ^{definitely} that the retention of all three types of resins was interfered with by the residues (6). It is assumed that the residues form fine particles^t with the resins which are ~~insoluble~~ ^{insoluble} and that these particles pass through the wire along with the white water.

KJELDAHL NITROGEN DETERMINATION
OF WET STRENGTH RESINS

Because urea formaldehyde and melamine formaldehyde resins contain ^{refractory}~~refractory~~ ring type nitrogen, the most generally accepted quantitative determination of the retention of the resins is based on the Kjeldahl nitrogen determination. Since the wet strength resins are composed of molecules that are of different chain lengths, this method is suitable only when separate resin nitrogen determinations can be made, and then considerable research is necessary because of the different chain lengths of the resins in which the nitrogen of one portion may vary considerably from the nitrogen of another portion of the same sample (17).

In determining the nitrogen content of a given sample according to the Kjeldahl method of determination, the two most important factors were pointed out by Shirley and Becker (11), ~~who~~ found that the type of catalyst and length of digestion time varied the results considerably.

Mercury and mercury plus selenium oxy-chloride were found to give the best results when used as a catalyst in the determination of the nitrogen content of compounds containing ~~refractory~~ ring type nitrogen. It was also found that when using these catalysts, a digestion time of from three to four hours was sufficient to complete the digestion (11).

The method for Kjeldahl determinations as described by TAPPI (12), may be used to determine the nitrogen of glue, ~~casein~~, urea formaldehyde resin, melamine resin, and other difficultly oxidized nitrogen compounds. This method is a modification of the Kjeldahl det-

~~ermination~~. The nitrogen compounds to be determined by this method ~~does not~~ include nitro~~s~~ ~~or~~ nitrates but does include ammonical nitrogen.

The principle of this modified method is based on the conversion of the ammonical nitrogen to ammonium sulphate during the digestion period. The ammonium sulphate is then mixed with an excess of sodium hydroxide and ammonium hydroxide is formed. The mixture is then heated and ammonia gas is distilled from the strongly basic solution and is collected in a flask containing a known amount of standardized acid. After the distillation has been completed, the excess acid in the flask is titrated with standardized sodium hydroxide and the percentage of nitrogen is determined. It is recommended that a blank determination of the procedure be conducted first using only the chemicals to determine the nitrogen content of the reagents.

The following procedure is a modification of the Kjeldahl determination as recommended by the Technical Association of the Pulp and Paper Industry.

Apparatus - A Kjeldahl distillation and digestion apparatus is required for this determination. An 800 ml Kjeldahl flask is the suitable size. Tight fitting stoppers and efficient Kjeldahl connecting bulbs should be used in the distillation.

Reagents - A. Sodium sulphate, c.p. Anhydrous, powdered.
 B. Metallic mercury or mercuric oxide, c.p.
 C. Selenium oxychloride, c.p.
 D. Sulphuric acid, c.p. conc.
 E. Zinc, granulated or stick.

F. Sodium Hydroxide solution, approximately 50% by weight (dissolve 1030g in 1L water).

G. Sulphide or thiosulphate solution: any of these may be used; 40g K_2S or 40g Na_2S or 80g $Na_2S_2O_3 \cdot 5H_2O$ / L H_2O .

H. Methyl red indicator, 1% alcoholic solution.

I. Standard sulphuric or hydrochloric acid, 0.1N accurately standardized.

J. Standard sodium hydroxide, 0.1N, standardized against the standard acid, using methyl red as an indicator.

Test specimen - The specimen shall consist of 2g A.D. paper the moisture content determined according to T412M. The specimen may be obtained by cutting small strips from different portions of the test sample in such a way as to represent the sample. The strips shall be cut into pieces approximately 6mm (0.25 in.) square.

Procedure - Weigh sample within 1mg accuracy. Place the sample in a Kjeldahl flask. Add 10g of anhydrous powdered sodium sulphate, 0.15g (5 drops) of selenium oxychloride, about 0.5g metallic mercury (0.55g mercuric oxide), and 25ml concentrated sulphuric acid. Place a small glass funnel in the neck of the flask, heat gently under a hood over a flame until the frothing has ceased and digest with increasing temperature until the oxidation is complete. This requires from one to two hours, after solution becomes clear and colorless.

Cool and dilute with 300-325 ml water. Add 2g of stick or granulated zinc to prevent bumping (stick may be used for several distillations) and 2ml of sulphide or thiosulphate (when $Na_2S_2O_3$ is used, mix with the sodium hydroxide so they may be added together).

Add 50% sodium hydroxide so as to obtain 5ml excess (this usually requires 55ml). Pour the sodium hydroxide down the neck of the flask so it does not mix with the acid, total volume should equal 400ml.

Immediately connect the flask to a condenser having the discharge end of its delivery tube just below the surface of a measured amount of 0.1N sulphuric or hydrochloric acid diluted to 100ml (25ml 0.1N acid is usually sufficient). mix the contents of the Kjeldahl flask by swirling the flask, slowly at first and then more rapidly. Start heating the flask immediately and distill the contents for about forty-five minutes, taking care to avoid spurting. the total volume of the distillate should equal 200ml.

Titrate the contents of the receiver flask with 0.1N sodium hydroxide, using methyl red indicator. Make a blank determination by conducting the entire procedure using only the reagents. Calculate the percentage of nitrogen by the formula;

$$\% \text{ Nitrogen} = \frac{(V_2 - V_1) \times N \times 0.014 \times 100}{W}$$

Where; V_1 = ml of sodium hydroxide used to titrate distillate from determination.

V_2 = ml of sodium hydroxide used to titrate distillate from blank.

N = Normality of the standardized sodium hydroxide solution.

W = Weight in grams of sample on moisture free basis.

Report - The percentage results should agree within 0.02% for duplicate determinations. The amount of nitrogen shall be expressed as the percentage of the moisture free paper to the nearest 0.01. If the desired report of a specific organic material is required, the percentage will be multiplied by the appropriate factor.

As these factors vary with different kinds and grades of material, they should be determined whenever the nitrogenous material is available and whenever possible the nitrogen in the paper should be determined before the addition of the nitrogenous material and subtracted from the total nitrogen found. The factors are not applicable when more than one nitrogenous material is present.

The Effect of Freeness of Unbleached Sulphite pulp
on the Retention of Wet Strength resins

Experimental Work

June 5, 1952

Submitted by

Walter J. Redmond

The Effect of Freeness of Unbleached Sulphite Pulp on the Retention of Wet Strength Resins

Much work has been done to substantiate the theories of the ionic character of the pulp fibers. These theories were developed in connection with the application of rosin, fillers, and dyes. Authors state that the problems of retention of wet strength resins are similar to those encountered when using rosins, fillers, and dyes (8,9). It is a well substantiated fact that by decreasing the freeness of various pulps, an increase in retention of various chemicals being used may be expected. This is also true when wet strength resins are being considered.

This fact could be explained by a closer inspection of the cellulose molecule. The anionic electrostatic charge of the pulp fibers is due to the carboxyl and hydroxyl groups present in the cellulose chain. The carboxyl groups are present in the extreme end of the cellulose chain, while the hydroxyl groups are located along the length of the cellulose chain. By decreasing the length of the cellulose chain, a carboxyl group is formed at the end of each segment. By fibrillation, the number of exposed hydroxyl groups along the length of the chain is increased. By decreasing the chain lengths and by fibrillation, the anionic nature of the pulp fibers is increased. This in turn increases the fibers receptivity for wet strength resins and other chemicals.

When unbleached pulps are used, the anionic character of the pulp is not due primarily to carboxyl and hydroxyl groups that are present. The electrostatic charge is due, however, to sulphonated lignin groups, which exhibit a stronger charge. When the freeness of un-

bleached pulps is decreased by beating, the anionic character of the pulp is not increased to any considerable degree. Even though more hydroxyl and carboxyl groups are exposed, the amount of sulphonated lignin groups is not increased.

The resins under study were cationic urea formaldehyde, anionic urea formaldehyde, and cationic melamine formaldehyde. Since resins cannot be compared with each other on the basis of retention, the experimental work was not carried out to prove or disprove the merits of each resin. The work was done to study a specific factor affecting the retention of the resins.

The pulp used for sheets was fifty percent hardwood and fifty percent softwood unbleached sulphite. The pulp was beaten for different time intervals of 10, 20, 30, and 40 minutes. Three percent resin was added in each case and was allowed one hour retention time to assure a definite equilibrium between the resins and the fibers. Three percent alum was also added and the pH was maintained at 4.5. All retention determinations were made with a Kjeldahl apparatus, according to TAPPI T-418-50. Duplicate determinations were made of each sample. Results of the experimental work are recorded on the following page.

Table 111

Beating Time (Minutes)	Freeness (cc)	Cationic Urea-form.	Anionic Urea-form.	Melamine Formaldehyde
10	570	57%	53%	70%
20	455	55%	53%	70%
30	240	53%	51%	71%
40	90	53%	55%	70%

The effect of freeness of unbleached sulphite pulp
on the retention of wet strength resin

Summary

Duplicate results of the ammonia present in a sample should agree within .2% . This means that duplicate results of the resin present in the same sample should agree within 1.0-1.5%, depending on the conversion factor of the resin. Since the results obtained from experimentation , plus or minus one percent, are very close, it is shown that the resin retention exhibited no definite trend to increase or decrease as the freeness of the unbleached sulphite pulp was decreased.

It is therefore shown that the freeness of unbleached sulphite pulp is not a critical factor in the retention of wet strength resins.

Submitted by

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