Fig. 2.
This invention relates to the manufacture of resin-treated cellulosic fibers and fibrous materials prepared therefrom, and is directed particularly to a method for improving the wet strength of felted fibrous cellulosic materials such as paper, board, shaped paper articles and the like. The invention includes the improved cellulosic fibers and fibrous product themselves as well as methods of preparing these products from aqueous suspensions of fibrous cellulosic materials such as paper pulp.

It has been known for some time that the wet tensile strength and the bursting strength of paper can be increased by soaking the formed paper in strong solutions of urea-formaldehyde resin, followed by heating the paper to evaporate the water and cure the resin. In some paper mills the urea-formaldehyde resin solution has been applied by spraying the solution onto a moving web of paper, followed by passing the paper over or between heated drying rolls. However, experience has shown that the impregnation of a formed sheet of paper with a resin solution, followed by curing the resin causes brittleness in the paper with a corresponding reduction in its folding endurance. Moreover, the evaporation of the additional water introduced with the resin requires a second heating of the paper if it has not been dried, or, if the paper is impregnated while it is still wet, a material reduction in the speed of the drying drums. Despite these objections, however, the so-called “tub” treatment of preformed paper with relatively concentrated aqueous solutions of synthetic resins is still used in some paper mills for special purposes, and the thermo-setting resins hereinafter described may be applied by this method within the broader scope of the present invention if desired.

In order to avoid the difficulties inherent in tub treatment, more recent practice in most paper mills manufacturing wet strength paper has been to apply a melamine-aldehyde resin of a special type, known as colloidal cationic melamine-aldehyde resin. The discovery that this type of resin possesses substantive properties for paper stock, and can be applied to dilute paper pulp suspensions in small quantities with a high degree of retention and excellent wet strength in the finished paper, was made jointly with Charles S. Maxwell by one of the present applicants. The details of this method of producing wet strength paper are described in an article in the August 9, 1945 issue of the Paper Trade Journal. Briefly, melamine-formaldehyde resin is dissolved in a water solution of hydrochloric acid or another strong acid other than sulfuric acid to form a solution containing about 0.8 mol of acid for each mol of melamine and the solution is aged, whereby polymerization takes place and a blue base develops, indicating the presence of resin particles in the colloidal range. This colloidal solution is added to the water suspension of paper stock in the beater bath chest, Jordan engine, head box or at any other suitable point ahead of the papermaking wire or screen. The stock is then formed into paper by the usual procedure and carried over steam-heated drying rolls which dry the paper and cure the resin to a water-insoluble condition.

It is a principal object of the present invention to provide papermaking fibers and paper impregnated with a thermosetting urea-formaldehyde resin capable of imparting wet strength thereto, which resin can be applied to the water suspension of hydrated paper stock in the beater, stock chest, head box or at any other suitable point ahead of the paper-forming step as is now done with the colloidal cationic melamine-aldehyde resin described above. Certain practical advantages are obtained by applying urea-formaldehyde resins instead of melamine-formaldehyde resin, notably the problem of broke recovery is greatly simplified when a urea-aldehyde resin is used. Moreover, urea-formaldehyde resins are at present considerably cheaper than the melamine-aldehyde resins; therefore, the process of the present invention provides a feasible means of producing wet strength paper by the so-called beater addition process at a reduced raw material cost.

We have found that the above and other objects are accomplished by applying to fibrous cellulosic material such as paper pulp an uncured thermosetting cationic urea-formaldehyde resin.

We have found that the resins of this class are substantive to fibers of cellulosic material such as paper pulp in aqueous suspension; i.e., the resin is selectively adsorbed or absorbed by the cellulosic fibers from a dilute aqueous solution or dispersion thereof containing these fibers in amounts much greater than those corresponding to the concentration of resin in the solution or to what would be contained in the water normally left in the sheet after forming. The importance of this discovery is evident, for it permits the application to cellulosic fibers of sufficient quantities of a thermosetting urea-formaldehyde resin capable of imparting wet strength while the fibers are in dilute aqueous suspensions of the consistency used in paper mills, which is
about 0.1-6% or, in special processes, at higher consistencies.

The cationic urea-formaldehyde resins which are applied to paper or paper stock by the process of our invention are prepared by condensing a urea-formaldehyde resin product under acid conditions, and preferably at pH values below 4.0-4.5, in the presence of a cationic nitrogen-containing organic compound that is capable of condensing with dimethyleneamines or other urea-formaldehyde reaction products are water-soluble polyfunctional organic nitrogen bases; i.e., compounds having the ability to copolymerize with urea-formaldehyde under acid conditions. Typical examples of such polyfunctional organic bases are the alkylenepolyamines of the formula \( H_2N(C_2H_{4}HN) \_x \) in which \( x \) is one or more such as ethylenediamine and 1,3-propylenediamine and polyalkylenepolyamines such as diethylenetriamine, triethylenetetramine, tetraethylenepentamine, the corresponding propylenepolyamines, and polybutylenepolyamines, also condensation products of alkyleneamines (such as the above) with halohydroxins such as alpha-dichlorhydrin, epichlorhydrin and the like, monosilylalkamines, dialkylamines and the like and the water-soluble condensation products thereof with aldehydes such as formaldehyde. By condensing these and similar polyfunctional cationic organic bases with dimethyl urea and similar primary or substantially monomeric urea-formaldehyde condensation products obtained by condensing urea or thiourea with formaldehyde, preferably under slightly alkaline conditions, with the addition of sufficient acid to reduce the pH to values of about 1.0 to 4.0, and preferably about 1.0 to 2.5, measured after the reaction has proceeded for some time, there are obtained cationic urea-formaldehyde resins which are substantive towards hydrated paper stock and can be used in the process of our invention.

It is an important feature of the cationic urea-formaldehyde resins prepared as described above that only relatively small proportions of the polyfunctional organic base need be used to obtain the desired cationic properties. The importance of using only small quantities of the basic material is two-fold; usually the organic bases such as polyalkylenepolyamines are more expensive than corresponding amounts of urea and formaldehyde, also relatively large quantities would tend to solubilize the thermosetting urea-formaldehyde resin and thus prevent the formation of a water-insoluble bond between the fibers of the felted paper. In fact, we find that resins containing a larger quantity of organic base than of urea, on a weight basis, possess little or no wet strength-imparting properties. Resins containing a smaller quantity of organic base than of urea, on the other hand, will impart wet strength to paper, and the wet tensile strength increases steadily as the ratio of organic base is decreased to the point where the resin syrups become hydrophobic in character and precipitate upon dilution with water. Accordingly, the preferred resins used in practicing the process of the present invention are those which contain about 2-30% of the organic base, calculated on the weight of urea used, and quantities of 6% to 15% are usually employed.

The cationic urea-formaldehyde resins applied to paper or paper stock by the process of the present invention are preferably prepared by first reacting urea with a methylene-yielding substance such as formaldehyde, paraformaldehyde or hexamethylenetetramine in known manner to form a primary urea-formaldehyde condensation product which is usually designated by resin chemists as dimethyl urea. This primary reaction product is preferably formed under neutral or slightly alkaline conditions, the latter being obtained by the addition of a small quantity of basic material such as sodium hydroxide or triethanolamine. A suitable polyfunctional organic base is then added as such or after it has first been reacted with formaldehyde and the resin solution is acidified by the addition of hydrochloric acid, nitric acid or other strongly acidic material to reduce the pH to the polymerizing range, which is about 1-4 and preferably 1-2. The resin syrup is then further reacted or polymerized, preferably at elevated temperatures on the order of 70°-90°C., in order to bring about a polymerization or copolymerization of the urea-formaldehyde and organic base and thereby produce a cationic resin.

The degree of polymerization of the cationic resin is an important factor. Tests have shown that much greater wet strength is obtained when the cationic resin is polymerized to a stage wherein a definite increase in its viscosity has been obtained, and the most efficient resins for wet strength purposes are those having a degree of polymerization corresponding to a viscosity of at least 100 centipoises in a resin syrup of 45% resin solids. Accordingly, we prefer to continue the resin polymerization, by holding the acidified syrups at appropriate temperature ranges as will hereinafter be more definitely explained, until a viscosity on the order of 100 centipoises or higher is obtained. The polymerized resin syrup is then preferably neutralized to a pH on the order of about 6-7 in order to obtain a product which is stable on storage. Resin syrups prepared by this method are both water-soluble and water-dilutable, and also can be evaporated to dryness and redissolved in water without substantial reduction in their water solubility or utility for the production of wet strength paper.

As has been stated, the cationic urea-formaldehyde resins can be applied to paper or other felted cellulosic products by tub application methods if desired. Thus, for example, preformed and completely or partially dried paper prepared from a chemical pulp such as sulfate, neutral sulfite, rag soda or sulfate or a mechanical pulp such as groundwood or any mixture thereof may be immersed in a 1% to 10% aqueous solution of the resin and impregnated with about 50-100% thereof, based on the weight of the paper. The paper is then heated for about 1-4 minutes at temperatures of 212°-300° F. or higher, or for shorter times at higher temperatures, whereby the paper is dried and the resin is cured to a water-insoluble condition. The resulting paper has greatly increased wet strength, and therefore this method is well suited for the impregnation of paper towels, absorbent tissue and the like as well as heavier stock such as wrapping paper, bag paper and the like to impart wet strength characteristics therefor.

The preferred process of the present invention, however, takes advantage of the substantive properties of the cationic urea-formaldehyde resins for hydrated cellulosic fibers. In practicing this process the resin in its uncured and hydrophilic or water-dilutable condition is added to an aqueous suspension of the paper stock, such as any
of those enumerated above, in the heater, stock
chest, Jordan engine, fan pump, head box or any other suitable point ahead of the paper-
making wire or screen followed by forming the
fretted fibers into a felted product on the wire
or cylinder. Ordinarily about 0.5% to 5% or
more of the resin solids, based on the dry weight of
the paper stock, is added in this manner.

The felted product is then heated in the usual
manner to dry the paper or board, thereby cur-
ning the resin to its polymerized and water-in-
soluble condition and imparting wet strength to the paper.

As noted above, the thermosetting cationic
urea-formaldehyde resins impart substantial wet
strength to paper and other products formed of
fretted cellulosic fibers when suitable amounts are
incorporated therein. The quantity of resin to be
added to the aqueous stock suspension will
depend on the degree of dry and wet strength
desired in the finished product and on the per-
cent of resin retained by the paper fibers. Thus,
as is shown in Example 1, the addition to the
aqueous paper stock suspension of as little as
0.75% produces a wet strength many times
greater than that of the untreated paper. Even
smaller quantities on the order of 0.1%, based
on the dry weight of the paper, may be used in
some cases. Ordinarily about 0.5% to 2% of
the resin is introduced into the paper and for
special purposes, as much as 3% to 5% of resin may be
incorporated therein. The resin not adsorbed
by the paper stock may be reused by employing
a circulating white water system; i.e., by using a
part or all of the white water from the paper-
making machine for preparing further batches of paper pulp suspension.

We have found that the uncured cationic
urea-formaldehyde resins contained in paper,
whether introduced as a tub size or combined
with the cellulosic fibers prior to sheet forma-
tion by adsorption in aqueous suspension, can
be cured under neutral or acid conditions by
subjecting the paper to a heat treatment.
However, the fastest cure and the best wet
strength are obtained by curing the resin under
slightly acid conditions, and therefore it is
preferable to acidify the paper stock before, during
or after the resin addition thereto. In most
cases this acidification can be advantageously
accomplished by the addition of about 1-3% of
aluminum sulfate (alum) which is frequently
used for the purpose of fixing resin or wax sizes in
the paper and therefore entails no added ex-
 pense. Under these conditions, wet strength is
imparted by a cure of 1-2 minutes at 220°-
260° F., or for shorter periods at higher tempera-
tures. The degree of wet strength is frequently
further increased by longer heating at normal
curing or lower temperatures, and this can be
obtained for example by storing the finished pa-
per from the drier section in roll whereby the
heat of the paper is utilized to cure the resin.

As is noted above, the retention of the cationic
resin by the paper fibers and the wet strength
developed in the finished sheet are greatly im-
proved by the addition of paper strength.
This partial polymerization is accomplished by acidi-
yfying the primary urea-formaldehyde condensa-
tion product, or dimethylol urea, to pH values
below 4.0-4.5, and preferably about 1.0-2.5, and
heating the acidified material with the cationic
monomeric or low molecular weight organo-
meric compound at poly-
merizing temperatures. Any suitable acid
capable of producing the low pH desired may be
used for the acidification, such as hydrochloric
acid, sulfuric acid, nitric acid, and the like.

The optimum polymerization temperatures to
be employed are dependent to a certain extent
on the ratio of formaldehyde or other methyol-
yielding substance to urea; with urea resin syrups
prepared with up to about 2.5 mols of formalde-
hyde for each mol of urea any temperature up
to about 90° C., or up to the refluxing tempera-
ture of the resin syrup may be employed. In
syrups prepared from substantially larger quan-
tities of formaldehyde (i.e., from about 2.5 mols
of formaldehyde for each mol of urea and up)
the optimum polymerization temperatures are
below 70° C., and are preferably from about 35°-
40° C. to about 65° C.

The polymerization of the cationic resin is
most readily followed by measuring the viscosity
of the resin syrups, and in the following exam-
plies this viscosity is expressed in terms of syrups
containing about 45% resin solids. However, it
should be understood that the viscosity of these
syrups does not change greatly, for a given stage
of polymerization, with a change in resin solids
content from about 35% to about 50%, and there-
for the results stated in these examples are equally applicable to syrups polymerized at some-
what lower resin solids content. The improve-
ments obtained with a representative cationic
urea-formaldehyde resin as a result of increased
polymerization are illustrated in the accompany-
ing drawings, in which.

Fig. 1 is a graph showing the increase in re-
tention of the cationic urea-formaldehyde resin
with an increase in viscosity up to about 100 cen-
tipoises, with a corresponding increase in the wet
strength of the paper.

Fig. 2 is a similar graph showing the rapid
polymerization of the resin by aging acidified
resin solutions of 45% resin solids at elevated
temperatures below 65°-70° C.

Although the following specific examples may
describe in detail certain specific features of the
invention, they are given primarily for purposes
of illustration and the invention in its broader
aspects is not limited thereto.

**EXAMPLE 1**

A mixture of 30 grams (0.5 mol) of urea, 81
grams (1 mol) of 37% aqueous formaldehyde so-
lution and 1 cc. of triethanolamine was heated
at 70° C. for 15 minutes, after which 3.8 grams
(0.02 mol) of tetraethylenepentamine and 4 cc.
of concentrated hydrochloric acid were added.

Heating was then continued at 70° C. for about 1
hour, or until a partially polymerized thermo-
setting urea-formaldehyde resin having cationic
properties was formed. The resulting resin syrup,
having a viscosity of about 150 centipoises, was
diluted with water to a 10% solution.

A sample of this resin syrup was further diluted
to 1% solids and tested for cationic properties by
a modification of the moving boundary method.
The dilute resin solution was poured into a test
cell having a horizontal portion, elliptical in cross-
section, into which platinum electrodes were
fused. Between the two narrow edges of the ground cotton fibers was suspended in
the resin solution. Upon passage of a direct current
through the electrodes at 60 volts the cotton plug
was observed through a microscope at a level
such that any movement of the liquid by electro-
sorption is zero, at that movement of the cot-
ton is a measure of its true charge.

The cotton fibers carrying the urea-formalde-

...
hyde-amine resin moved toward the negative electrode (cathode) at a rate of 1.02 cm. per second, thus showing the presence of a positive electrical charge on the resin particles. Bleached Kraft paper pulp was beaten in the usual manner and made into a 0.6% water suspension. Samples were treated with the above-described resin, in some cases with the addition of aluminum sulfate, and made into hand-sheets which were heated 1 minute at 230° F. to dry the paper and cure the resin. Some of the sheets were given an additional heating of 10 minutes at 260° F. to determine the effect of a more complete cure. The sheets were then tested for dry and wet tensile strength along with a sheet made from the same stock but containing no resin. In the following table, which shows the results obtained, the per cent of added resin solids and alum is based on the dry weight of the paper pulp; the per cent resin retained is based on the resin added, and the basis weight is the weight in pounds of 500 sheets 35 x 40 inches in size.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Percent resin added</th>
<th>Percent resin retained</th>
<th>Basis weight</th>
<th>Tensile strength, lbs./in.</th>
<th>Dry</th>
<th>Wet</th>
<th>Dry</th>
<th>Wet</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>None</td>
<td>None</td>
<td>48.7</td>
<td>22.0</td>
<td>0.6</td>
<td>21.8</td>
<td>0.6</td>
<td>21.8</td>
</tr>
<tr>
<td>2</td>
<td>0.73</td>
<td>3</td>
<td>50.7</td>
<td>22.0</td>
<td>1.2</td>
<td>22.6</td>
<td>1.2</td>
<td>22.6</td>
</tr>
<tr>
<td>3</td>
<td>1.5</td>
<td>3</td>
<td>51.2</td>
<td>22.6</td>
<td>1.8</td>
<td>22.6</td>
<td>1.8</td>
<td>22.6</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>3</td>
<td>52.0</td>
<td>22.2</td>
<td>2.6</td>
<td>22.4</td>
<td>2.6</td>
<td>22.4</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>3</td>
<td>54.6</td>
<td>24.2</td>
<td>3.2</td>
<td>23.2</td>
<td>3.2</td>
<td>23.2</td>
</tr>
<tr>
<td>6</td>
<td>7</td>
<td>3</td>
<td>55.0</td>
<td>24.8</td>
<td>3.8</td>
<td>23.2</td>
<td>3.8</td>
<td>23.2</td>
</tr>
</tbody>
</table>

1 After additional cure.

**EXAMPLE 2**

A mixture of 271.2 parts by weight of 37% aqueous formaldehyde, preferably methanol-free, and about 3 parts of triethanolamine is charged into a reaction vessel and stirred to a uniform solution. 80 parts by weight of urea are then added and mixed thoroughly. At this point the pH should be within the range of 8.3 to 8.8 and, if necessary, an adjustment is made by adding triethanolamine or formic acid. The mixture is then heated to 70° C. and held at that temperature for 15 minutes. The solution is then cooled to 65° C. and 8 parts by weight of tetraethylenepentamine are added followed by 12 parts of water. After again cooling to 65° C., a mixture of 12 parts by weight of 33% hydrochloric acid and 12 parts of water is added while maintaining the temperature of the batch at 70°C.

The pH of the reaction mixture should be followed at this point. Ten minutes after the acid addition it is usually 2.4 to 2.5 and drops to 1.7 to 1.8 within another 15 minutes. If, at this time, the pH is outside the limits of 1.0 to 2.0 it should be adjusted to a value within these limits by adding dilute hydrochloric acid or dilute sodium hydroxide.

The temperature of the batch is preferably maintained at 70°C. for one hour after addition of the hydrochloric acid, although a higher temperature and shorter reaction time may be used. It is then reduced, preferably to about 55°-60° C., and the viscosity of the resin solution is followed carefully. This reduction in the reaction temperature causes an increase in the viscosity. When a viscosity of 100-200 centipoises or higher has been reached the acid resin is neutralized immediately by adding 18 parts by weight of 10% sodium hydroxide solution. In most cases this will yield a resin having a pH of 6.8-7. Resin syrups prepared by this method are soluble in water at all concentrations and do not become hydroporphic even after several months storage at ordinary atmospheric temperatures (4° to 30° C.), and therefore require no ethanol or other extraneous organic solvents.

**EXAMPLE 3**

A resin solution prepared as described in Example 2 was used in a commercial mill trial under full-scale operating conditions. The stock was bleached Southern Kraft paper pulp beaten to a moderate degree of freeness and treated with 1.25% of its weight of resin size and sufficient alum (about 2%) to adjust the pH of the stock to 4.9 to 5.0. The concentrated resin solution was diluted with water to 10-20% resin solids and run to a constant head box and from there through a constant flow meter to the exhaust side of the fan pump, where it was mixed with the stock suspension. The amount of resin added was 1.64% of resin solids, based on the dry weight of the stock. The fourdriner machine was equipped with 12 drying rolls supplied with steam at 45 pounds gauge pressure followed by one Yankee supplied with steam at 30 pounds and two after-driers. The machine speed was 650 feet per minute.

Samples of the paper were taken at regular intervals and were tested for wet and dry tensile strength and other physical characteristics. Other samples were given an additional cure and subjected to the same tests. The test results were as follows:

**EXAMPLE 4**

Another mill trial was made on a fourdriner machine with the resin of Example 2. A 50-pound bag paper was made from unbleached Kraft paper pulp containing 0.34% of its weight of resin size and sufficient alum to maintain a pH of 4.2-4.5 in the white water. The production rate was 8.8 tons per hour at a machine speed of 990 feet per minute, the drying rolls being maintained at 268° F. The resin solution was done with water to a concentration of 1 pound resin solids per gallon and introduced at a uniform rate in an amount equal to 1.67% resin solids, based on the dry weight of the paper stock. Samples of the paper were taken at uniform intervals and tested for wet and dry tensile strength and other physical char-
The retention of the cationic urea-formaldehyde-amine resins by the cellulosic fibers, and the resulting wet strength on heating the formed cellulose articles to cure the resin, is greatly increased by partially polymerizing the resin. This can be accomplished by several methods. In urea resin syrups prepared with more than about 25 mols of formaldehyde or other melamine-yielding substances for each mol of urea, the polymerization takes place by continued heating at temperatures of about 70°-90° C. or higher after acidification to a pH value within the range of about 3-6.

Thus, for example, a resin syrup was prepared by reacting 1 gram mol of urea and 2 gram mols of aqueous 37% formaldehyde containing 2 grams of triethanolamine at 70° C. for 15 minutes. To this there were added 8 grams of tetraethylenepentamine and a solution of 8 cc. of concentrated hydrochloric acid in 20 cc. of water, and the solution was heated at 70° C. After 5 minutes heating the pH was 4.1, and a viscosity increase was noticeable. The viscosity increased rapidly upon continued heating at the same temperature, indicating further polymerization of the resin, until eventually a stiff gel was formed.

In the next step, formaldehyde-amine resins prepared by reacting 2.5 mols or more of formaldehyde or equivalent quantities of paraformaldehyde or other melamine-yielding substances for each mol of urea there is little or no increase in viscosity after the first 30 minutes of heating under acid conditions at temperatures of 70° C. or higher. However, the viscosity increase can be continued to the desired range in these resin solutions by lowering the temperature below 70° C.; preferably to about 45°-65° C., and continuing the reaction at these reduced temperatures. This is shown by the following:

Four resin syrups were prepared by reacting, in each case, 4 gram mols of urea with 10 gram mols of 37% aqueous formaldehyde containing 8 cc. of triethanolamine and having a pH of 8.5 at 70° C. for 15 minutes. 24 grams of tetraethylenepentamine were then added followed by 28.5 cc. of concentrated hydrochloric acid in 85 cc. of water and the heating was continued at 70° C. After 30 minutes heating the resin solids content was about 45% and the pH value was 1.8 in all the syrups. Heating was continued at 70° C. for an additional 30 minutes, at which time samples were withdrawn, neutralized by the addition of 20% NaOH solution, and the viscosity at 70° C. was found to be 60 centipoises. The solutions were then treated as follows:

Solution A was cooled to 50° C. in 2 minutes and held at this temperature for 10 minutes.

Solution B was cooled to 50° C. in 2 minutes and held at this temperature for 4 minutes.

Solution C was cooled to 60° C. in 2 minutes and held at this temperature for 12 minutes.

Solution D was maintained at 70° C. for 12 minutes.

A sample of each solution was withdrawn every 2 minutes, neutralized with 20% NaOH solution, and tested for viscosity.

The results of these tests are shown on Fig. 2 of the drawings. These results show that the dimethylurea-amine resins were polymerized in acidified aqueous solutions at temperatures of 60°, 55° and 50° C. at constantly increasing rates, but that practically no further polymerization takes place upon continued heating at 70° C.

The importance of partial polymerization of the resin in the production of wet strength paper is evident from the curves shown on Fig. 1 of the drawings. The data shown on these curves were obtained by withdrawing portions of the resin solution of Example 2 prior to and during the final polymerization stage at 55°-58° C., immediately neutralizing them and determining their viscosity, and then adding them in amounts of 3% resin solids, based on the dry weight of the fiber, to 1% aqueous suspensions of kraft paper pulp. The pulp suspensions were then made into hand sheets which were analyzed for resin content and tested for wet strength. The curves show that a rapid increase in the resin retention with a corresponding increase in wet strength is obtained as the polymerization of the resin increases to a stage corresponding to a viscosity of 60-70 centipoises, measured at 25° C., in a 45% resin solution. Above this stage there is only a slight increase in retention with continued polymerization and practically no increase in wet strength.

EXAMPLE 6

Resin No. 1

A solution of 240 grams (4 mol) of urea in 811 grams (10 mols) of aqueous 37% formaldehyde was adjusted to a pH of 8.5 by the addition of 20 cc. of a 50% aqueous triethanolamine solution and was then heated at 70°-74° C. for 30 minutes. Thirty-two grams of dicyandiamide were added and then 55 cc. of 18.4% hydrochloric acid, the pH after the acid addition being 2.0, and heating was continued at 70°-75° C. for 55 minutes during which time the pH rose to 4.0. After cooling and adjusting the pH to 3.5 by adding an additional 1 cc. of hydrochloric acid solution, the solution was aged at 45°-55° C. for 1.5 hours and then neutralized by adding sodium hydroxide solution. The viscosity of the resulting quaternary-modified urea-formaldehyde resin syrup was 220 centipoises.

Resin No. 2

Urea ........................................ 120
37% formalin .............................. 406
50% triethanolamine solution .......... 8
50% epichlorhydrin-TEPA aqueous resin solution ........................................ 12
Water ........................................ 20
HCl (17.7%) ................................ 12

The epichlorhydrin resin solution was prepared by adding the epichlorhydrin slowly to a water
solution of the tetraethylenepentamine with stirring while maintaining the temperature at about 50° C. followed by continued reaction at the same temperature as described in Example 1 of the copending application of Daniel and Landes, Serial No. 689,334 filed August 3, 1946, now Patent No. 2,565,838, but using equimolecular quantities of epichlorhydrin and tetraethylenepentamine.

The primary urea-formaldehyde resin syrup was prepared and the epichlorhydrin resin solution and hydrochloric acid were added, using the procedure described for Resin No. 1. The pH was 2.8 after adding the hydrochloric acid, and dropped to 2.0 after heating at 70°–50° C. for 30 minutes. After raising the pH to 3.3 by adding NaOH the syrup was aged at 55°–57° C. for 35 minutes to a viscosity of 250 centipoises and then neutralized with 10% NaOH solution.

Resin No. 3

Grabs

<table>
<thead>
<tr>
<th>Component</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urea</td>
<td>250</td>
</tr>
<tr>
<td>Formalin, 37% aqueous</td>
<td>311</td>
</tr>
<tr>
<td>Diethylenetriamine</td>
<td>24</td>
</tr>
<tr>
<td>HCl (18%)</td>
<td>54</td>
</tr>
</tbody>
</table>

The urea was dissolved in the formalin, the pH was adjusted to 8.5 by adding 1.7 cc. of 10% NaOH solution, and the solution heated at 70°–75° C. for 30 minutes. It was then cooled to 65° C, and the diethylenetriamine, dissolved in 50 grams of water, was added and the temperature increased to 70° C. The hydrochloric acid was then added (pH after addition being 4.3) and the mixture was maintained at 70°–75° C. for 1 hour. During the first 25 minutes of this period the pH dropped steadily until it reached 1.7, at which point it remained constant during the rest of the heating period.

After heating for 1 hour the pH was raised to 3.0 by adding 8 cc. of 10% NaOH solution and the solution was cooled to 50°–55° C. and aged at this temperature for 15 minutes. It was then neutralized to a pH of 7 by adding 10% NaOH solution. The viscosity of the resin syrup was 200 centipoises.

Resin No. 4

Grabs

<table>
<thead>
<tr>
<th>Component</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urea</td>
<td>180</td>
</tr>
<tr>
<td>Formalin, 37% aqueous</td>
<td>608</td>
</tr>
<tr>
<td>Diethanolamine</td>
<td>16</td>
</tr>
<tr>
<td>HCl (17.7%)</td>
<td>37</td>
</tr>
</tbody>
</table>

The procedure of Resin No. 3 was followed, the solution being held at 60°–65° C. for 25 minutes after adding the diethanolamine and HCl and aged at 50°–55° C. to a viscosity of 370 centipoises. The neutralized resin syrup was soluble in a mixture of equal parts of water and ethanol.

Resin No. 5

The quantities and procedure of Resin No. 3 were used, but 52 grams of quaternal hydrochloride were substituted for the diethylenetriamine and 16.4 grams of 18.4% HCl were used to obtain a pH during heating of 1.45. The syrup was aged 30 minutes at 40–45 degrees to a viscosity of 140 centipoises and neutralized to a pH of 7 with NaOH.

Samples of the above cationic resins were added to beaten kraft paper pulp in amounts of 3% resin solids, based on the dry weight of the paper pulp, and handsheets were made and tested for wet and dry tensile strength as described in

Example 1. The results are given in the following table:

<table>
<thead>
<tr>
<th>Resin No.</th>
<th>% resin retained</th>
<th>Basis weight</th>
<th>Tensile strength, lbs./in. width</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25</td>
<td>24.7</td>
<td>26.6, 1.6, 22.4, 3.2</td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>25.3</td>
<td>21.2, 4.4, 22.9, 6.9</td>
</tr>
<tr>
<td>3</td>
<td>15</td>
<td>21.2</td>
<td>25.4, 4.6, 27.2, 6.8</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>18.4</td>
<td>22.6, 3.3, 27.8, 6.0</td>
</tr>
</tbody>
</table>

Example 2

Air inlet temp., °C.----------

Example 7

Another important advantage of resin sprays prepared by the method of the present invention is the fact that they can be evaporated to dryness without impairing substantially either their water solubility or their substantive properties towards hydrated paper stock. Thus, for example, a sample of the tetraethylenepentamine-urea-formaldehyde syrup of Example 2 was evaporated to dryness at room temperature and the resulting white solid was ground. The ground material was redissolved in water and added to a 50% suspension of beaten kraft paper stock, which was then made into handsheets that were heated in the usual manner to cure the resin. The resulting paper had good wet strength.

Samples of the resin syrup of Example 2 were also spray-dried at a feed rate of 100 cc. per minute in a spray dryer equipped with a jacketed nozzle feeding the resin solution to a rotating spray wheel. The temperature conditions were as follows:

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Air inlet temp., °C</th>
<th>Air outlet temp. °C</th>
<th>Analysis of direct resin</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>230</td>
<td>200</td>
<td>225</td>
</tr>
<tr>
<td>2</td>
<td>250</td>
<td>200</td>
<td>225</td>
</tr>
</tbody>
</table>

Percent solids | 92.2 94.4 97.7
Percent nitrogen | 24.4

The spray-dried resin was obtained as a fairly dense, dry product, about 95% of which was readily soluble in water. Complete solution was obtained in water containing a small quantity of hydrochloric acid or other acid, the amount being such that a 10% solution of the resin had a pH of 5–6.

These resins were tested for use in the manufacture of wet strength paper by the procedure described in Example 1, using 3% of the resin and 3% of alum, based on the weight of the paper stock, with bleached kraft pulp at a pH of 4.5. The cure was one minute at 230° F.; “condition of resin” indicates the condition in which the resin was added to the paper pulp suspension. The following test data were obtained:

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Condition of resin</th>
<th>% resin retained</th>
<th>Basis weight</th>
<th>Tensile strength, lbs./in. width</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10% sola.</td>
<td>48</td>
<td>49.4</td>
<td>26.0, 5.3</td>
</tr>
<tr>
<td>2</td>
<td>10% sola.</td>
<td>47</td>
<td>49.3</td>
<td>25.6, 5.8</td>
</tr>
<tr>
<td>3</td>
<td>10% sola.</td>
<td>45</td>
<td>47.8</td>
<td>24.3, 4.0</td>
</tr>
<tr>
<td>4</td>
<td>10% sola.</td>
<td>43</td>
<td>50.5</td>
<td>23.4, 3.4</td>
</tr>
<tr>
<td>5</td>
<td>10% sola.</td>
<td>42</td>
<td>48.3</td>
<td>22.6, 3.2</td>
</tr>
<tr>
<td>6</td>
<td>10% sola.</td>
<td>41</td>
<td>49.4</td>
<td>22.6, 3.2</td>
</tr>
</tbody>
</table>

These results show that the spray-dried urea-formaldehyde-amine resins can be added in the
beater, stock chest or elsewhere ahead of the paper-making wire or screen either as a dry powder or after dissolving in water with results comparable to those obtained with the resin syrups before spray drying.

**EXAMPLE 8**

A series of resin syrups was prepared with varying ratios of tetraethylenepentamine to urea, as follows:

<table>
<thead>
<tr>
<th>Resin No.</th>
<th>TEPA</th>
<th>Urea</th>
<th>Formamidelethion 35% solution</th>
<th>Ratio TEPA to Urea</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Grams</td>
<td>Mols</td>
<td>Grams</td>
<td>Mols</td>
</tr>
<tr>
<td>1. 1-a</td>
<td>69</td>
<td>0.23</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2. 4</td>
<td>47</td>
<td>0.22</td>
<td>11.25</td>
<td>1.25</td>
</tr>
<tr>
<td>3. 35.5</td>
<td>33.5</td>
<td>1.0</td>
<td>11.25</td>
<td>1.25</td>
</tr>
<tr>
<td>4. 23.75</td>
<td>23.75</td>
<td>0.8</td>
<td>55.75</td>
<td>5.52</td>
</tr>
<tr>
<td>5. 17.75</td>
<td>17.75</td>
<td>0.6</td>
<td>67.50</td>
<td>6.75</td>
</tr>
<tr>
<td>6. 10.0</td>
<td>10.0</td>
<td>0.4</td>
<td>82.50</td>
<td>8.25</td>
</tr>
</tbody>
</table>

Resin No. 1 was prepared by adding the formaldehyde slowly to the tetraethylenepentamine and heating for one hour at 70°C, 140°F, of the resin. In Resin No. 1—s the same procedure was followed, but sufficient hydrochloric acid was added before heating to lower the pH to about 2. Resins Nos. 2—6 were prepared by the procedure described in Example 2, i.e., by first reacting the urea and formaldehyde under slightly alkaline conditions, then adding the tetraethylenepentamine and sufficient hydrochloric acid to give a pH of about 3, continuing the condensation for another 30 minutes and holding for a viscosity of about 150—155 centipoises or higher, and neutralizing with sodium hydroxide.

Handsheets were made from bleached kraft stock using 3% of the above resins, based on the dry weight of the stock. The pH of the stock suspension was adjusted to 4.5 by the addition of alum, except where otherwise noted. The sheets were given an ordinary cure of one minute at 230°F, and some were also given an extra cure of 10 minutes at 260°F, and all were tested for wet and dry tensile strength. The results are given in the following table.

<table>
<thead>
<tr>
<th>Resin No.</th>
<th>TEPA for % resin</th>
<th>Percent resin retained</th>
<th>Basis weight</th>
<th>Tensile strength, lbs./in. width</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dry</td>
<td>Wet</td>
<td>Dry</td>
<td>Wet</td>
</tr>
<tr>
<td>1</td>
<td>8</td>
<td>8</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>2</td>
<td>14</td>
<td>14</td>
<td>14</td>
<td>14</td>
</tr>
<tr>
<td>3</td>
<td>18</td>
<td>18</td>
<td>18</td>
<td>18</td>
</tr>
<tr>
<td>4</td>
<td>22</td>
<td>22</td>
<td>22</td>
<td>22</td>
</tr>
<tr>
<td>5</td>
<td>26</td>
<td>26</td>
<td>26</td>
<td>26</td>
</tr>
<tr>
<td>6</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
</tr>
</tbody>
</table>

These results show clearly that the ratio of amine to urea should be maintained below 1:1 and that best results are obtained when it is 0.3:1 or lower; in fact, good results have been obtained with as little as 2 grams of tetraethylenepentamine to 60 grams of urea. The tetraethylenepentamine—formaldehyde condensation product itself (Resins Nos. 1 and 1-a) produces no increase in wet strength; therefore it is important to use only sufficient of the amine to impart the necessary cationic properties to the urea formaldehyde resin. Experience has shown, however, that the resin syrups become unstable upon dilution to 10% resin solids or less when the quantity

of tetraethylenepentamine is lowered to less than about 7 per cent of the weight of urea used; therefore the preferred quantity is about 4 to 10 grams for each 60 grams of urea for the preparation of syrups in which stability after dilution is desired. When the resin syrups are to be used without prior dilution the amount of polyalkylamine or other urea and formaldehyde-reactive amine may be reduced to as low as 2–3% of the weight of the urea while retaining the cationic properties of the resin.

**What we claim is:**

1. A process for the production of wet strength paper which comprises adding to an aqueous suspension of cellulose paper stock a partially polymerized, hydrophilic cationic urea—formaldehyde resin obtained by condensing dimethyl urea and a quantity of an alkylene polyamine which is about 6% to 15% of the weight of the urea in said dimethyl urea at a pH below 4.5 and polymerizing the condensation product to a degree corresponding to a viscosity of at least 100 centipoises in a 45% aqueous solution thereof, adsorbing about 0.1% to 5% of said resin on said paper stock, forming the stock so treated into a waterlaid sheet, and heating the sheet for about 1–4 minutes at 212°F to 300°F and thereby forming a bond of cured resin between the fibers theretof.

2. A process for the production of wet strength paper which comprises adding to an aqueous suspension of cellulose paper stock a partially polymerized, hydrophilic cationic urea—formaldehyde resin obtained by condensing dimethyl urea and a quantity of a polyalkylene polyamine which is about 6% to 15% of the weight of the urea in said dimethyl urea at a pH below 4.5 and polymerizing the condensation product to a degree corresponding to a viscosity of at least 100 centipoises in a 45% aqueous solution thereof, adsorbing about 0.1% to 5% of said resin on said paper stock, forming the stock so treated into a waterlaid sheet, and heating the sheet for about 1–4 minutes at 212°F to 300°F and thereby forming a bond of cured resin between the fibers theretof.

3. A process for the production of wet strength paper which comprises adding to an aqueous suspension of cellulose paper stock a hydrophilic cationic urea—formaldehyde—polyfunctional organic nitrogen base resin which is partially polymerized to a degree corresponding to a viscosity of at least 100 centipoises in a 45% aqueous solution thereof, said resin containing a quantity of polyfunctional organic nitrogen base which is within the range of 6% to 15% of the weight of the urea therein, adsorbing about 0.1% to 5% of said resin on said paper stock, forming the stock so treated into a waterlaid sheet, curing said resin to its heat-set and water-insoluble condition by heating it for about 1–4 minutes at 212°F to 300°F, and thereby forming a bond of cured resin between the fibers of said paper.

4. A process for the production of wet strength paper which comprises adding to an aqueous suspension of cellulose paper stock a hydrophilic cationic urea—formaldehyde—polyfunctional organic nitrogen base resin in which the amount of polyfunctional organic nitrogen base is 2–30% of the weight of the urea, adsorbing about 0.1% to 5% of said resin on said paper stock, forming the stock so treated into a waterlaid sheet, and curing said resin to its heat-set and water-insoluble condition by heating said
sheet for about 1–4 minutes at 212°F to 300°F, and thereby forming a bond of cured resin between the fibers of said paper.

5. The process for the production of wet strength paper, which comprises adding to an aqueous suspension of cellulosic paper fiber a hydrophilic, cationic urea-formaldehyde-triethyleneetramine resin in which the triethyleneetramine is 6% to 15% of the weight of the urea, absorbing about 3% based on the fiber of said resin on the fiber, forming the stock so treated into a waterlaid sheet, then heating the sheet for about 100 seconds at 121°F, and thereby forming paper of increased wet strength.

6. A method of producing wet strength paper which comprises applying to the fibers thereof about 0.1% to 5% by weight of a partially polymerized, hydrophilic cationic urea-formaldehyde-polyfunctional organic nitrogen base resin in which the amount of polyfunctional organic nitrogen base is 2–30% of the weight of the urea and then curing said resin to its heat-set and water-insoluble condition by heating the paper for about 1–4 minutes at 212°F to 300°F, and thereby forming a bond of cured resin between the fibers of said paper.

7. A method of producing wet strength paper which comprises applying to the fibers thereof about 0.1% to 5% by weight of a partially polymerized, hydrophilic cationic urea-formaldehyde-polyfunctional organic nitrogen base resin in which the amount of polyfunctional organic nitrogen base is about 6% to 15% of the weight of the urea and then curing said resin to its heat-set and water-insoluble condition by heating the paper for about 1–4 minutes at 212°F to 300°F, and thereby forming a bond of cured resin between the fibers of said paper.

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CHESTER G. LANDES.
TZENG JUEQ SUIEN.

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<th>Name</th>
<th>Date</th>
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</tr>
</tbody>
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