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FABRICATION OF WET-STRENGTHENED PAPER

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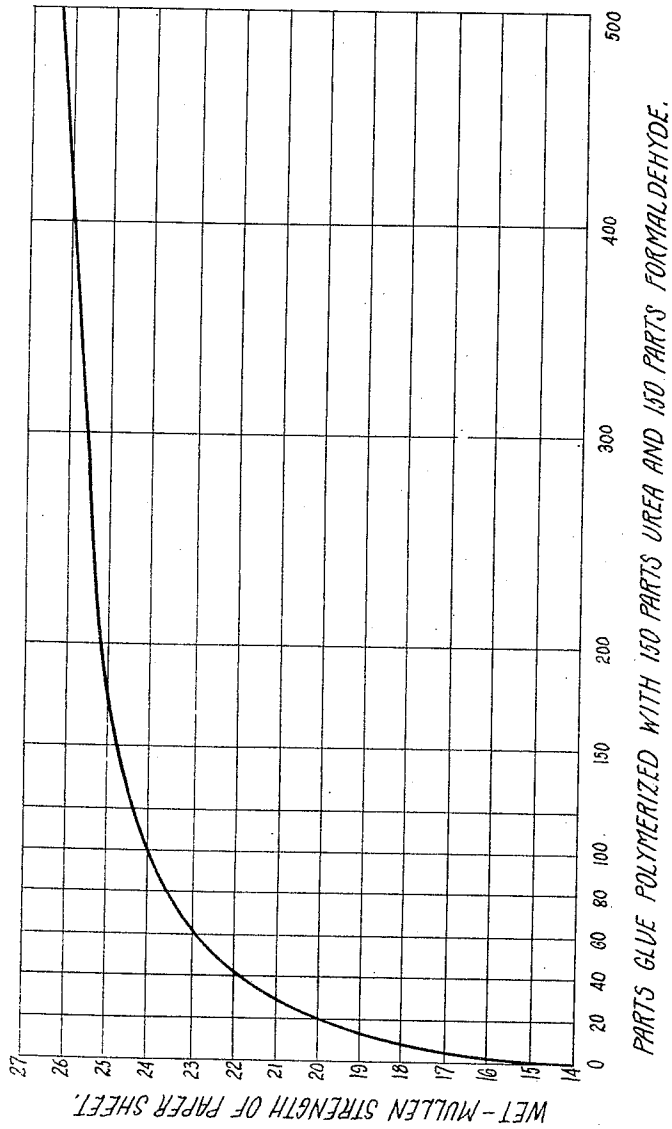

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FABRICATION OF WET-STRENGTHENED PAPERS

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12 Claims. (Cl. 92—21)

This invention relates to the fabrication of wet-strengthened papers, that is, papers characterized by their high strength while wet with water. While not limited thereto, it deals more especially with paper products characterized by their high water absorptivity as well as their high wet-strength and hence particularly adapted for use wherein both such qualities are prized, e. g., as toweling, handkerchiefs, facial tissues, napkins, toilet paper, diaper linings, dress shields, etc.

The polymer or condensation product of urea and formaldehyde has been found to be an excellent wet-strengthening agent for paper, especially when a still-liquid or fluent aqueous urea-formaldehyde polymer composition is incorporated into the papermaking stock and the paper sheet fabricated from such stock is subjected to a suitable after-heating treatment, such as described in my co-pending application Serial No. 226,330, filed August 23, 1938, which has since become abandoned. Paper products of both high absorptivity and wet-strength may be produced by the use of a limited amount of the urea-formaldehyde polymer or condensation product; and a paper product of surprisingly high wet-strength results from such after-heating treatment of the paper sheet as is described in that application even when a very small amount, say, as little as about 1% to ⅛% urea-formaldehyde polymer, is present in the sheet. The method of that application is hence a very economical one in that the cost of the urea-formaldehyde polymer necessary for attaining a particular wet-strength value much greater than that of a similar paper sheet lacking the polymer is low.

As set forth in my co-pending application Serial No. 226,330, filed August 23, 1938, a urea-formaldehyde condensation product is made by reacting urea and formaldehyde in aqueous solution and carrying the reaction to the stage where the viscosity of said solution has risen sharply and is in the course of mounting rapidly but has not reached the gel stage. The reaction is arrested when the viscosity of the solution is in the range thus defined and the solution is incorporated with a paper furnish prior to the formation of a web therefrom. Acid conditions promote the fixation of the polymer or condensation product on the fiber. Thus, for example, the furnish may be brought to an acidic condition as indicated by a pH value of about 4 to 5, by the use of an acidic reagent of which alum is a specific example.

By carrying the reaction between urea and formaldehyde in aqueous solution to the viscosity stage described, the polymer or condensation product is not only readily dispersible throughout the furnish but is also well retained on the fibers and it thus becomes possible to employ very small proportions of the condensation product in relation to the dry weight of the pulp in the furnish, and by subjecting the formed web to a suitable curing or after-heating treatment high wet-strengths may be obtained even though the proportion of condensation product incorporated with the furnish is very small in relation to the dry weight of the pulp in the furnish. For example, while a typical range of proportion of condensation product is ⅛ of 1% to 5%, high wet-strengths may be obtained with as little as ⅛ of 1% to 1% when the formed web is subjected to a suitable curing or after-heating treatment. The preferred curing or heat treatment is that set forth in my United States Patent No. 2,116,544 issued May 10, 1938, in accordance with which the formed web or sheet after forming and drying on a papermaking machine is exposed momentarily, e. g., for about one second, to a temperature of about 450° to 500° F., which may be accomplished by running the sheet progressively from the dry end of the paper-making machine over a roll periphery heated to the stated temperature range. The curing treatment may, however, involve heating for a substantial period of time at temperatures of about 150° to 300° F. as, for example, by winding the paper as it is delivered hot from the dry end of the paper-making machine on a roll and storing the roll at such elevated temperatures for a period of, say, five minutes to twenty-four hours so as to develop the desired high wet-strength quality in the finished paper product.

In accordance with the description in co-pending application Serial No. 226,330, the urea-formaldehyde polymer useful for the purposes hereof may advantageously and typically be prepared by cooking 100 parts of urea with aqueous formaldehyde solution containing 120 parts of formaldehyde (CH_2O), 203 parts of plain water, and 27 parts of 28% ammonia water at, say, about 190° to 200° F., in a loosely covered vessel until the viscosity of the aqueous solution or mixture has mounted considerably above that of the initial aqueous mixture or composition and is in the course of mounting rapidly but is definitely short of the jelly state. The resulting clear aqueous polymer composition is preferably cooled immediately after its preparation to retard or arrest further polymerization and thus to keep such composition in the still-liquid condition desired for addition to the papermaking stock. Since the urea-formaldehyde polymer

composition is quite viscous and of low heat-conductivity and since the polymerizing reaction is proceeding rapidly under the elevated temperature prevailing therein, the arresting or checking of further polymerization presents technical difficulty when attempted by ordinary expedients, such as indirect cooling of the hot composition. I have found, however, that the desired arresting or checking of the polymerization reaction in the composition may be achieved readily by adding a water-miscible alcohol, such as ethyl alcohol, to the hot composition, preferably through a pipe at a region of submergence in a body or pool of the hot composition, in which case the alcohol distributes itself rapidly throughout the body or pool and, as it boils and spreads uniformly throughout the composition, quickly cools the composition throughout and checks undesirable further polymerization in the composition by virtue of both its quick cooling effect and its inhibiting effect on the polymerizing reaction. Various other water-miscible organic liquids capable of arresting the polymerizing reaction may be added in lieu of alcohol to the hot composition; and it is preferable that such organic liquids be of lower boiling point than water to accomplish additionally the desired quick cooling and mixing action on the composition, by virtue of the boiling of such organic liquids in the hot composition, which is at a temperature higher than the boiling point of such organic liquid added thereto. The addition of the alcohol or equivalent organic liquid may be accomplished while the organic liquid vapors are being emitted into a reflux condenser and are thereby condensed and returned to the body of the composition. Sufficient alcohol or equivalent organic liquid may be added to the hot composition to lower its temperature markedly within a few moments; and further cooling to approximately room temperature can then be accomplished gradually, as in the reaction vessel or in the containers into which the still-warm composition may be delivered. A typical procedure may involve the addition of about 100 parts of ethyl alcohol to a composition prepared from proportions of materials and otherwise as described in the example hereinbefore given, that is, to the resultant composition of the foregoing example while such composition is at a temperature of about 190° to 200° F., in which case the composition is very rapidly cooled to a temperature of about 170° F., which is sufficiently low to ensure against gelling of the alcohol-containing composition upon its further cooling by mere exposure to the prevailing atmosphere. The cooled composition may without gelling or loss of effectiveness for the purposes hereof be stored for days, or even weeks. While the alcohol or equivalent reaction arrester may be added to the hot polymer composition at normal or room temperature, it may in some instances be refrigerated or cooled to distinctly subnormal temperature preparatory to its addition to the polymer composition. The cooled composition is practically clear, readily pourable, and very easily dispersible or mixable in water.

When the aqueous urea-formaldehyde polymer composition is mixed with the comparatively large amount of water of the papermaking stock or pulp suspension, the alcohol or other water-miscible organic liquid added to arrest polymerization in such composition diffuses practically entirely throughout such water; and the polymer affixed to the stock by alum or other fixative is thus practically free from the alcohol or other organic water-miscible liquid.

The reaction between urea and formaldehyde is preferably carried out by employing about two molecular proportions of free formaldehyde to one of urea in the presence of an alkaline substance as, for example, ammonia or amines. As also set forth in application Serial No. 226,330, it is possible to dispense with an ammoniacal or basic promoter of the condensing and polymerizing reaction between urea and formaldehyde in aqueous solution and to use in lieu thereof such reaction promoters as glue, casein and similar albuminous or proteinous substances.

After the polymer composition has been incorporated with the papermaking furnish, sufficient acidic reagent may be added to the furnish to render it distinctly acid, for instance, to bring the pH value to about 4 to 5. The resulting acidic stock after dilution with water to suitable papermaking consistency is then delivered to a papermaking machine and formed into a sheet.

I have now found that the cost of making wet-strengthened paper products may be further reduced while enhancing the wet-strength quality of such products by compounding with the urea-formaldehyde polymer incorporated into such products an albuminous binder of the nature of animal glue. While not limited thereto, it is preferable to accomplish such compounding in the course of preparing the urea-formaldehyde polymer, for instance, in accordance with the method of preparing urea-formaldehyde polymer disclosed in my co-pending application Serial No. 226,329, filed August 23, 1938, which has since become abandoned, according to which application glue or like albuminous or proteinous substance is used as a promoter and/or participant of the reaction in an aqueous admixture of urea and formaldehyde leading to an aqueous polymer composition useful to excellent advantage in producing wet-strengthened paper products. It is evidently the case that the three substances, namely, urea, glue, and formaldehyde interact with one another to form a urea-glue-formaldehyde polymer or compound; and, aside from the fact that the glue has been found to promote the desired reaction between the urea and formaldehyde and to influence such reaction in the direction of yielding aqueous polymer compositions of the desired fluency, clarity, and other qualities, it has been found to contribute importantly toward enhancing conspicuously the wet-strength of the paper product containing such urea-glue-formaldehyde polymer over a similar paper product containing a similar amount of urea-formaldehyde polymer (i. e., polymer prepared in the absence of glue or equivalent albuminous material). The enhanced wet-strength realized in any particular paper product containing the urea-glue-formaldehyde polymer, by virtue of the glue component of such polymer, has been found to depend upon the particular amount of glue forming part of the polymer; and the more glue entering into such polymer up to a particular point, the greater the wet-strengthening action on a particular paper product of the urea-glue-formaldehyde polymer. In accordance with the present invention, therefore, the urea-glue-formaldehyde polymer incorporated into the papermaking stock may vary in its content of glue from a low percentage to a very high percentage, even though there is ordinarily no advantage to be gained in increasing the glue content more than 100% by weight of the urea-

formaldehyde mixture by reason of the fact that the wet-strengthening effect of the glue on a paper product containing the urea-glue-formaldehyde polymer increases sharply up to a glue content of about 50%, based on the weight of the urea-formaldehyde mixture, then increases relatively much more slowly up to a glue content of about 100%, based on the weight of the urea-formaldehyde mixture, and then remains substantially constant at higher percentages of glue content.

The urea-glue-formaldehyde polymer to be used accordant with the present invention in the fabrication of wet-strengthened paper products may be prepared in the manner disclosed in my application Serial No. 226,329. Thus, as disclosed in that application, the procedure may be to dissolve a suitable animal glue, for example, the hide glue known on the market as "Peter Cooper's No. 5," in about eight times its weight in water, to mix the glue solution with about 150 parts by weight of urea, and to heat the resulting urea-glue solution to about 195° F. Into about 150 parts by weight of formaldehyde in the form of an aqueous solution also heated to about 195° F. (e. g., the usual commercial formalin solution containing 37.5% formaldehyde and small quantities of such impurities as methyl alcohol and formic acid) may be trickled or progressively added the hot urea-glue solution at such regulated rate as to maintain gentle ebullition in the mixture, wherein ebullition occurs because of the exothermic reaction between the urea and formaldehyde. The progressive addition of the urea-glue solution to the formaldehyde solution may be completed in about 30 minutes, whereupon the resulting substantially clear aqueous composition or mixture may be maintained hot, say, at a temperature of about 190° to 200° F., in a water bath or a water-jacketed tank until its viscosity has risen sharply and is in the course of mounting rapidly. The time of heating necessary for promoting polymerization and thickening of the aqueous urea-glue-formaldehyde mixture to the desired degree short of gelling may be about one hour after the addition of the urea-glue solution to the formaldehyde solution has been completed. Further polymerization in the hot, still-clear, aqueous urea-glue-formaldehyde polymer composition is arrested quickly by adding thereto, as its viscosity is rapidly increasing, a suitable amount of alcohol, acetone, or equivalent water-miscible organic liquid, as described in application Serial No. 226,329.

The aqueous, urea-glue-formaldehyde polymer composition may be incorporated into papermaking stock, as in the beater engine, and the polymer discharged on the stock by the addition of alum or other suitable fixative. Not only is the polymer readily disseminated or dispersed substantially uniformly throughout the papermaking stock at the usual beater consistency, say, about 3% to 5%, but the retention of the urea-glue-formaldehyde polymer by the papermaking stock upon the addition thereto of alum or equivalent fixative is excellent. After the polymer has been admixed substantially uniformly with the stock, sufficient alum or its equivalent may be added to bring the stock to distinctly acidic condition, for instance, to a pH value of about 4.0 to 5.0. It is generally best to dilute the aqueous urea-glue-formaldehyde polymer composition with two or three volumes of hot water before adding it to the stock in the beater engine, for the undiluted composition may tend to develop insoluble matter when added directly to cold water. The excellent retention of the polymer by the fibers of the papermaking stock is believed to be the result of adsorption rather than of mechanical entrainment, such as may occur to a large extent when rosin or wax size is precipitated by alum on papermaking stock in the usual way or when raw or cooked starch is admixed with papermaking stock. This conclusion as to the adsorption of the polymer by the pulp fibers appears to be warranted by the observation that when the polymer is properly admixed with water in the absence of pulp fibers, no directly apparent or sensible precipitant or turbidity, attributable to the polymer, may be developed in the water even upon the addition thereto of alum in such amount as causes the polymer to be adsorbed very largely or substantially completely by pulp fibers in aqueous suspension, as already indicated.

Depending upon the particular kind of paper product desired, various amounts of the urea-glue-formaldehyde polymer may, pursuant to the present invention, be incorporated into the papermaking stock. As little as about ⅛% to 1% of the polymer, based on the dry weight of fiber, is all that need be added to make papermaking stock intended for absorptive paper products, such as toweling made more especially from semi-bleached or unbleached wood pulps of the character of kraft pulp, but papermaking stock intended for tougher and denser paper products may be charged with a large amount of the polymer, say, about ⅔ to 4%, based on the dry weight of fiber. Stock intended for such purposes as toweling need undergo very little, if any, beating prior to the formation of paper, whereas stock intended for fabrication into tougher and denser paper products such as are useful for wrapping or holding moist or wet vegetables, for lining crates in which iced lettuce or similar produce is to be shipped, etc., may be well-beaten. Even in the case of such latter paper products, however, it is preferable to use as a maximum less than about 5% of the polymer, based on the dry weight of fiber, for the use of more than such amount of polymer may embrittle the finished paper product unduly and may depreciate its dry tear-resistance to an undesirable extent. In speaking about a particular percentage of the polymer, based on the dry weight of fiber, the percentage is calculated in terms of non-aqueous material, that is, the dry urea, glue, and formaldehyde entering into the preparation of the polymer even though the polymer is prepared and added to the fiber in the form of an aqueous polymer composition.

After the urea-glue-formaldehyde polymer has been admixed with the papermaking stock and the stock rendered distinctly acidic with alum or equivalent acidic reagent or salt, a paper sheet may be formed from the stock by the usual practice, which involves dilution of the stock with water to the desired papermaking consistency on its way to the papermaking machine. After a dried paper sheet of a basis weight suitable for the particular purpose or use in view has been fabricated, it is subjected to an after-heating treatment appropriate for the development of the desired high wet-strength quality therein, as described in my application Serial No. 226,330. For instance, the paper sheet may be exposed

for about one second to a temperature of about 450° to 500° F., as by running the sheet progressively from the dry end of the papermaking machine over a roll periphery heated to such temperature so as to yield a finished paper product of the desired high wet-strength; or it may be heated for a substantial period of time at comparatively moderately elevated temperatures, say, about 150° to 300° F., as by winding it as it is being delivered hot from the dry end of the papermaking machine into a roll and maintaining or storing the paper roll at such elevated temperature for a period of, say, five minutes to twenty-four hours so as to develop the desired high wet-strength quality in the finished paper product. Other suitable modes of after-heating the polymer-containing paper in dried condition may be adopted.

Using the particular procedure hereinbefore given in preparing the urea-glue-formaldehyde polymer, including the particular proportions of urea and formaldehyde cited therein, and plotting as abscissae various proportions of glue used in the preparation of the polymer and as ordinates the wet-Mullen or bursting strength values of sheets of forty-pound basis weight into which 1% of the polymer, based on the dry weight of fiber, was incorporated and which was subjected in dry condition to an after-heating or "hot-shot" treatment at 460° F. for 1.3 seconds, the curve shown on the accompanying drawing was obtained. This curve plainly shows the material advantage to be gained in using glue, up to a certain point, as a reactant or reaction promoter in the polymerization of aqueous urea-formaldehyde mixtures, so far as concerns increasing the wet-strength of paper products into which the resulting polymer is incorporated and which have been subjected to suitable heat-treatment in dried condition.

The principles of the present invention apply to paper products containing various proportions of the urea-glue-formaldehyde polymer. In a finished paper product containing a particular percentage of polymer, the higher the glue content of the polymer up to a certain point, which is generally about 50% of the weight of the urea-formaldehyde mixture, the greater will be the wet-strength quality of the paper product. In preparing a polymer for the purposes hereof, it is preferable to avoid a substantial amount of free formaldehyde during the latter stages of the polymer-forming reaction. Such a condition prevails during the polymer-forming reaction hereinbefore described, according to which about two mol-proportions of formaldehyde are mixed with one mol-proportion of urea. The mol-ratio of formaldehyde to urea is in any event preferably maintained less than about 3 to 1, for instance, within a range of about 2 to 1 to about 3 to 1. Should more than such mol-ratio of formaldehyde to urea be used in preparing the polymer, namely, a mol-ratio greater than about 3 to 1, provision is preferably made for removing the excess or free formaldehyde before or during the polymerizing stage of the reaction, that is, the stage during which the reaction product undergoes rapid thickening or increase in viscosity. It might be noted that the initial stage of the reaction is attended by comparatively little, if any, thickening of the mixed reacting ingredients.

The preparation of the urea-glue-formaldehyde polymer compositions useful for the purposes hereof may without disadvantage be varied in such respects as the use of thio-urea or substituted ureas or thio-ureas in lieu of the urea and the use of acetaldehyde or other higher aldehydes in lieu of the formaldehyde. Accordingly, the term "urea" employed in the appended claims is meant to include the indicated chemical equivalents of urea; and, similarly, the term "formaldehyde" employed in the appended claims is meant to include various aldehydes that react with urea-glue mixtures in much the same way as formaldehyde to yield urea-glue-aldehyde polymers. The term "glue" is used herein and in the appended claims to mean not only animal glue of the nature of hide glue and fish glue but also similar albuminous or proteinous substances, such as hemoglobin, casein, etc. The instant invention is subject to various further modifications without departing from its spirit or scope as defined by the appended claims, including the possible omission of the step of subjecting the paper product in dried condition to an after-heating or "hot-shot" treatment. In this latter connection, it might be noted that the use in paper products of urea-glue-formaldehyde polymer compositions accordant with the present invention conduces to products of greatly enhanced wet-strength even when such products are simply dried, that is, are not subjected to an after-heating or "hot-shot" treatment. However, it is distinctly preferable, in accordance with the present invention, to subject the paper product in dried condition to an after-heating or "hot-shot" treatment, as such a treatment not only augments pronouncedly the wet-strength of the product but utilizes the full value of the glue component of the urea-glue-formaldehyde polymer in developing or bringing to fruition a finished paper product having a greater wet-strength than a product similarly made and containing a similar amount of urea-formaldehyde polymer (i. e., a polymer lacking a glue component) is realized.

This application is a continuation-in-part of my copending application Serial No. 226,330, filed August 23, 1938.

I claim:

1. The process of making paper which comprises reacting urea and formaldehyde in aqueous solution; carrying the reaction to the stage where the viscosity of said solution has risen sharply and is in the course of mounting rapidly but has not reached the gel stage; incorporating said solution with a paper furnish prior to the formation of a web therefrom, and forming paper from said furnish under acid conditions.

2. The process of making paper which comprises reacting urea and formaldehyde in aqueous solution; carrying the reaction to the stage where the viscosity of said solution has risen sharply and is in the course of mounting rapidly but has not reached the gel stage; incorporating said solution with a paper furnish, prior to the formation of a web therefrom, in an amount sufficient to provide a proportion of the urea-formaldehyde reaction product of about ⅛ of 1% to about 5% of the dry weight of the pulp in the furnish, and forming paper from said furnish under acid conditions.

3. The process of making paper which comprises reacting urea and formaldehyde in aqueous solution; carrying the reaction to the stage where the viscosity of said solution has risen sharply and is in the course of mounting rapidly but has not reached the gel stage; incorporating said solution with a paper furnish, prior to the forma-

tion of a web therefrom, in an amount sufficient to provide a proportion of the urea-formaldehyde reaction product of about ⅛ of 1% to about 1% of the dry weight of the pulp in the furnish, and forming paper from said furnish under acid conditions.

4. The process of making paper which comprises reacting urea and formaldehyde in aqueous solution; carrying the reaction to the stage where the viscosity of said solution has risen sharply and is in the course of mounting rapidly but has not reached the gel stage; incorporating said solution with a paper furnish prior to the formation of a web therefrom and acidifying said furnish, and forming paper from said furnish.

5. The process of making paper which comprises reacting urea and formaldehyde in aqueous solution; carrying the reaction to the stage where the viscosity of said solution has risen sharply and is in the course of mounting rapidly but has not reached the gel stage; incorporating said solution with a paper furnish, prior to the formation of a web therefrom, in an amount sufficient to provide a proportion of said urea-formaldehyde reaction product of about ⅛ of 1% to about 5% of the dry weight of the pulp in the furnish, and acidifying said furnish, and forming paper from said furnish.

6. The process of making paper which comprises reacting urea and formaldehyde in aqueous solution; carrying the reaction to the stage where the viscosity of said solution has risen sharply and is in the course of mounting rapidly but has not reached the gel stage; incorporating said solution with a paper furnish, prior to the formation of a web therefrom, in an amount sufficient to provide a proportion of said urea-formaldehyde reaction product of about ⅛ of 1% to about 1% of the dry weight of the pulp in the furnish, and acidifying said furnish, and forming paper from said furnish.

7. The process of making paper which comprises reacting urea, formaldehyde and glue in aqueous solution; carrying the reaction to the stage where the viscosity of said solution has risen sharply and is in the course of mounting rapidly but has not reached the gel stage; incorporating said solution with a paper furnish prior to the formation of a web therefrom, and forming paper from said furnish under acid conditions.

8. The process of making paper which comprises reacting urea, formaldehyde and glue in aqueous solution; carrying the reaction to the stage where the viscosity of said solution has risen sharply and is in the course of mounting rapidly but has not reached the gel stage; incorporating said solution with a paper furnish, prior to the formation of a web therefrom, in an amount sufficient to provide a proportion of the urea-formaldehyde-glue reaction product of about ⅛ of 1% to about 5% of the dry weight of the pulp in the furnish, and forming paper from said furnish under acid conditions.

9. The process of making paper which comprises reacting urea, formaldehyde and glue in aqueous solution; carrying the reaction to the stage where the viscosity of said solution has risen sharply and is in the course of mounting rapidly but has not reached the gel stage; incorporating said solution with a paper furnish, prior to the formation of a web therefrom, in an amount sufficient to provide a proportion of the urea-formaldehyde-glue reaction product of about ⅛ of 1% to about 1% of the dry weight of the pulp in the furnish, and forming paper from said furnish under said conditions.

10. The process of making paper which comprises reacting urea, formaldehyde and glue in aqueous solution; carrying the reaction to the stage where the viscosity of said solution has risen sharply and is in the course of mounting rapidly but has not reached the gel stage; incorporating said solution with a paper furnish prior to the formation of a web therefrom and acidifying said furnish, and forming paper from said furnish.

11. The process of making paper which comprises reacting urea, formaldehyde and glue in aqueous solution; carrying the reaction to the stage where the viscosity of said solution has risen sharply and is in the course of mounting rapidly but has not reached the gel stage; incorporating said solution with a paper furnish, prior to the formation of a web therefrom, in an amount sufficient to provide a proportion of said urea-formaldehyde-glue reaction product of about ⅛ of 1% to about 5% of the dry weight of the pulp in the furnish, and acidifying said furnish, and forming paper from said furnish.

12. The process of making paper which comprises reacting urea, formaldehyde and glue in aqueous solution; carrying the reaction to the stage where the viscosity of said solution has risen sharply and is in the course of mounting rapidly but has not reached the gel stage; incorporating said solution with a paper furnish, prior to the formation of a web therefrom, in an amount sufficient to provide a proportion of said urea-formaldehyde-glue reaction product of about ⅛ of 1% to about 1% of the dry weight of the pulp in the furnish, and acidifying said furnish, and forming paper from said furnish.

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