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(54) **Compositions for imparting temporary wet strength to paper.**

(57) A composition for imparting temporary wet strength to paper comprising a solution containing from about one percent to about ten percent by weight of a vinylamide polymer having sufficient glyoxal-reactive amide substituents and -CHOHCHO substituents to be thermosetting, in a solvent selected from the group consisting of water, water-miscible solvents containing free hydroxyl functionality, and mixtures thereof, to which solution has been added a sufficient quantity of a strong base for reaction therewith to adjust the pH of the aqueous solution to a value of from about 8.5 to about 11. Also disclosed is a process for imparting temporary wet strength to paper by application thereto of a wet strengtheningly effective amount of such aqueous composition, and the paper product of such process.

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COMPOSITION FOR IMPARTING TEMPORARY
WET STRENGTH TO PAPER

BACKGROUND OF THE INVENTION

Field of the Invention

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The present invention broadly relates to a composition and process for producing paper with enhanced wet strength characteristics, and specifically relates to a composition and process for imparting temporary wet strength to paper, and to the paper product of such process.

Description of the Prior Art

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In the general practice of papermaking, an aqueous pulp suspension, or "furnish", of cellulosic fibers resulting from pulping of feed wood stock is hydraulically and mechanically conveyed onto a wire grid or screen which is in motion to produce a wet web of cellulosic fibers.

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The wet fiber web is dewatered on the screen, by drainage of liquid therefrom, following which the wet web may be further treated, dried, calendared, and subjected to additional treatments as desired.

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Typically, a number of additives are contained in the furnish which is passed to the wire substrate wet web forming means. Such additives may include processing aids for improving operation of the papermaking machinery as well as paper chemicals for improvement of the properties of the finished paper product. One such class of processing aids is wet-strength additives.

Water-soluble polymers which have the property of imparting wet strength to paper are particularly commercially important and widely employed. Certain of these poly-

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mers, which may be nonionic or ionic, either anionic or cationic and which may be in a colloidal state develop their wet strength only under acid conditions, such as the materials disclosed in U.S. Patent Nos. 2,345,543; 2,582,840; 5 and 2,596,014. Due to the fact that such acid conditions can subject the paper-making equipment to corrosive conditions as well as the fact that the resulting paper product undergoes premature embrittlement, the use of hydrophilic vinylamide polymers which have sufficient -CHOHCHO substituents to be thermosetting have recently become popular. 10 These polymers possess the property of providing paper with wet strength rapidly at neutral pH conditions, with or without exposure to thermosetting temperatures, as disclosed in U.S. Patent No. 3,556,932.

15 As disclosed in the aforementioned U.S. Patent No. 3,556,932, water-soluble vinylamide polymers which are thermosetting by reason of a reactive content of glyoxal (as therein and hereinafter termed for convenience "vinylamide polymers which have sufficient content of -CHOHCHO substituents to be thermosetting") possess the important and advantageous property when applied to paper of losing a part of its wet strength when soaked in water for a moderate length of time. Such wet strength characteristic is highly useful for paper such as facial and other tissues, and paper towel- 20 ling, where permanent wet strength is a positive disadvantage. Nonetheless, such wet strength paper, in order to lose substantially all of its wet strength rapidly, requires the soaking of the paper in alkaline water.

25 It would be highly advantageous, and a significant advance of the art, to obtain a wet strength paper which is capable of losing substantially all of its wet strength rapidly in a neutral aqueous medium. 30

Accordingly, it is an object of the present invention to provide a composition for imparting temporary wet strength to paper, utilizing a water-soluble vinylamide polymer having sufficient -CHOHCHO substituents to be thermosetting.

It is a further object of the present invention to provide such composition for imparting temporary wet strength to paper, which has good shelf life, i.e., storage stability, for a period on the order of at least several months.

It is a still further object of the invention to provide paper with temporary wet strength and to a process for making same, using the improved wet strength composition of the present invention.

Other objects and advantages of the present invention will be apparent from the ensuing disclosure and appended claims.

SUMMARY OF THE INVENTION

In one aspect, the present invention relates to a composition for imparting temporary wet strength to paper, comprising an aqueous solution containing from about one percent to about ten percent by weight, based on the weight of solution, of a water-soluble vinylamide polymer having sufficient glyoxal-reactive amide substituents and -CHOHCHO substituents to be thermosetting, in a solvent selected from the group consisting of water, water-miscible solvents containing free hydroxyl functionality, and mixtures thereof, the ratio of the number of said -CHOHCHO substituents to the number of said glyoxal-reactive amide substituents being in excess of 0.06:1, to which has been added a sufficient quantity of a strong base for reaction therewith to adjust the pH of the solution to a value of from about 8.5 to about 11.

In order to impart enhanced shelf life, i.e., storage stability, to the above-described composition, it is preferred in practice to stabilize the aqueous solution by addition thereto of sufficient quantity of a mineral acid, such as hydrochloric, sulfuric or nitric acid, preferably hydrochloric acid, to adjust the pH of the solution to a value of from about 3 to about 4. Such acidification step is effective to increase the shelf life of the temporary wet strength composition from on the order of several

weeks which would otherwise be characteristic of the composition in the absence of such stabilization step to a storage life of at least several months.

5 The vinylamide polymer employed in the above-described composition may be in colloidal state in the aqueous solution. A particularly preferred polymer is a cationic water-soluble about 99:1 to 75:25 molar ratio acrylamide:diallyl dimethyl ammonium chloride polymer.

10 The preferred pH ranges in the strong base reaction step and the optional acidification/stabilization step are from about 9.0 to about 10.5, and from about 3.2 to about 3.8, respectively.

15 Various strong bases may be employed in the pH elevation base reaction step, although amines and ammonium hydroxide impart strong colors to the product paper which may in some applications be undesirable inorganic bases, such as potassium hydroxide and sodium hydroxide work well and are preferred in practice.

20 In another aspect, the instant invention relates to a process for imparting temporary wet strength to paper, comprising applying thereto a wet strengtheningly effective amount of the aforementioned aqueous composition. The application of the temporary wet strength composition to the paper substrate may be carried out in any suitable
25 manner as conventionally practiced in the art for wet strength resin treatments, such as by spraying of the aqueous composition to the final paper product, or alternatively by incorporation of the aqueous composition in the furnish at the "wet end" of the papermaking process.

30 In yet another aspect, the instant invention relates to a paper with temporary wet strength, having applied thereto a wet strengtheningly effective amount of the above-described aqueous composition..

DESCRIPTION OF THE INVENTION

The polymers employed in the temporary wet strength composition of the present invention are water-soluble polyvinylamides having sufficient -CHOHCHO substituents to

be thermosetting. Such polymers may be nonionic or ionic, either cationic or anionic.

5 The amount of ionic component in ionic polymers of the aforementioned type is that which is sufficient to render them self-substantive to cellulose fibers in aqueous suspensions (in the case of the cationic polymers, or to render them precipitable on cellulose fibers in aqueous suspensions by the action of alum (in the case of anionic polymers of the present invention). The proportions of
10 ionic groupings which need be present in such ionic polymers is small, generally less than 10 mol percent of the vinyl components of the polymer, if desired, however, a larger proportion may be present.

15 Whether or not sufficient ionic groupings (cationic or anionic) are present in the aforementioned ionic polymers can be determined in any instance laboratory trial, employing the methods shown in examples set forth hereinafter. Sufficient ionic groupings are present when upwards of 50% of the amount of polymer in any one instance
20 is retained by the fibers (as determined by analysis of the fibers for their nitrogen content before and after treatment).

A few ionic groupings per macromolecule are generally sufficient, and perhaps even one ionic substituent per macromolecule is enough. However, it is preferable for
25 the polymers to contain between 1 and 10 ionic groupings per 100 chain carbon atoms (e.g., 4 to 50 ionic substituents per macromolecule of 200 monomer units) because in this range the danger of too few ionic groups being present is
30 generally avoided, and consumption of the often more costly ionic component is minimized. The term "groupings" includes substituents.

The vinylamide content of the polymers of employed in the composition of the present invention provides the sites to which the glyoxal substituents (hereinafter designated "CHOHCHO substituents") are attached. The minimum proportion of vinylamide units which should be present in

any instance can be determined by laboratory trial; the proportion of these substituents should be sufficient so that the polymer (with -CHOHCHO substituents attached) is thermosetting, i.e., so that a film of the polymer laid
5 down from water solution on a glass plate and heated for 5 minutes at 105°C. is insoluble in water at room temperature.

The vinylamide units provide sites to which the -CHOHCHO substituents are attached and with which these substituents react during the thermosetting reaction.

10 About 10 mol percent of vinylamide units (based on the total number of vinyl monomer units present) appear to be the minimum needed to provide the necessary number of sites. It is usually advantageous for the proportion of these units to be much higher, large proportions promoting
15 the wet-strengthening properties of the polymer without conferring any significant off-setting disadvantage and avoiding the loss resulting from the presence of too low a proportion of these groups. It thus appears better for the vinylamide units to be present in major amounts, i.e., in
20 amount larger than 50 mol percent, and better still for the proportion of these units to be in excess of 75 mol percent. The remaining units in the polymers of the present invention may be units which confer ionic properties upon the polymer, which act as diluents or spacers, or which
25 confer special properties, for example, improved or diminished water-solubility.

The composition of the present invention comprises a vinylamide polymer in a solution whose solvent component is selected from the group consisting of water, water-
30 -miscible solvents containing free hydroxyl functionality, i.e. water-miscible alcohols and polyols, such as methanol, ethanol, ethylene glycol and propylene glycol. Alcohols are advantageous solvents for such solutions, particularly at higher vinylamide polymer concentrations, e.g. on the order of from about 5 to about 10 percent by weight (based on total solution weight), since alcohols appear to retard advancement (cross-linking reaction) of the polymer, there-

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by minimizing its advancement to a water-soluble gel (gelation).

5 The composition of the invention is prepared by addition of strong base to the vinylamide polymer solution, such addition being carried out at any suitable temperature as for example in the range of from about -10°C to about 75°C, with temperatures in the range of from about 15°C to about 35°C being generally satisfactory. At higher vinylamide polymer solids levels, e.g., on the order of
10 from about 5 percent to about 10 percent by weight, higher temperatures in the range of from about 25°C to about 75°C may be usefully employed to minimize the aforementioned advancement of the polymer.

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Excellent results have been obtained from the cationic water-soluble reaction products of glyoxal with polymers composed of acrylamide and diallyldimethyl ammonium chloride residues in molar ratio between 99:1 and 75:25; with polymers composed of methacrylamide and 2-methyl-5-vinylpyridine in 99:1 to 50:50 molar ratio; and cationic water-soluble polymers composed of vinyl acetate, acrylamide and diallyldimethyl ammonium chloride in about 8:40:2 molar ratio.

The polymers of the present invention are prepared from vinylamides which may have any molecular weight up to the point where they do not dissolve in water but instead merely form non-fluid gels. Such polymers are adequately water-soluble at molecular weights in the range of 100,000-1,000,000. Solutions thereof in water are not unduly viscous, and evidently these polymers may usefully possess still higher molecular weights. However, lower molecular weight polymers are more easily handled (because of their lower viscosity and easier water-dilutability) and when reacted with glyoxal they possess better storage stability. For these reasons, it is preferred to employ polymers having molecular weights less than 25,000 as starting materials. Such polymers contain roughly 200-300 monomer units per average macromolecule, of which about 150-200 units are vinylamide units.

The polymers of the present invention, as freshly prepared, are water-soluble and in most instances aqueous solutions thereof are clear, colorless, and sparkling and free from haze. The latter indicates that the polymeric molecules are substantially entirely hydrophilic and are of sub-colloidal dimensions. On standing at room or elevated temperature at 2%-5% solids, these solutions develop a blue opalescent haze having the appearance of that described in U.S. Patent No. 2,345,543, which shows that the macromolecules have attained colloidal dimen-

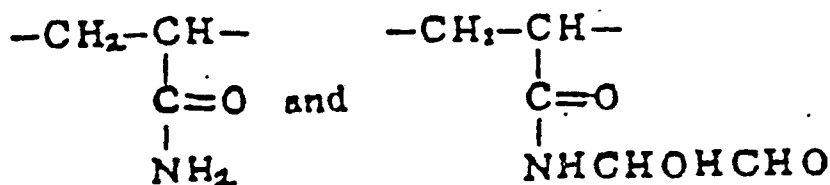
sions, evidently as the result of inter-molecular condensations.

5 In certain instances aqueous solutions of the polymers are hazy when freshly prepared. The cause of this haze has not been ascertained, but is generally caused by the presence of macromolecules which are not substantially entirely hydrophilic but which are on the borderline between being hydrophilic and hydrophobic (insoluble).
10 Such molecules contain hydrophobic linkages, for example, the residues of styrene, acrylonitrile, octadecyl acrylate, N-octyl acrylamide, etc., in sufficient number to place them on the borderline between water-solubility and water insolubility. The haze may be composed of colloidal particles or of colloidal aggregates of sub-
15 colloidal particles.

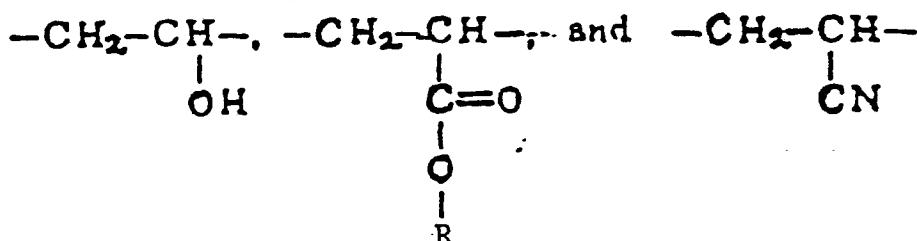
We have found that from the dimensional point of view, best wet strength is imparted by colloidal particles. In numerous instances we have found that the wet
20 strengthening property of a polymer increases by 10% to 15% when it has grown to colloidal dimensions. This increase in efficiency is obtained merely by permitting the polymer solutions to age until they develop a colloidal haze.

25 The time required by solutions of polymers of the present invention to develop a colloidal haze varies widely, depending on such variables as the molecular weight of the polyvinylamide employed as raw material, the concentration of polymer in the solution, the temperature
30 of the solution, and the pH of the solution. Most rapid development of the haze occurs when the starting polyamide, while clearly water-soluble, is of high molecular weight and contains hydrophobic substituents, when the concentration of polymer in the solution is high, and when the temperature and pH of the solution are high. Slow development of the colloid is favored by reversal of these conditions.

In perhaps their simplest, the polymers of the present invention can be composed of units having the theoretical formulae

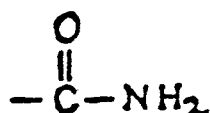


plus units which confer an ionic charge to the molecule. If desired, diluent units may be present, for example



(wherein R is hydrogen or lower alkyl)

units. Such units are tolerated in small amounts. It will be understood that the polymers may also contain linkages formed when the $-\text{CHOHCHO}$ substituents react with the

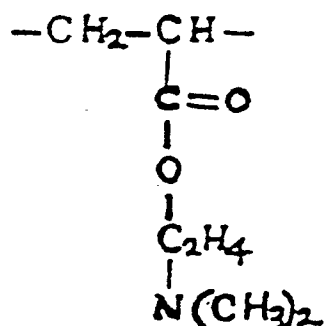


substituents, which occurs to a small extent during manufacture of the polymers.

In practice, the polymers of the present invention are generally most conveniently prepared by reacting a pre-formed ionic hydrophilic water-soluble polyvinylamide with sufficient glyoxal to form a water-soluble polymer which is thermosetting. Many suitable polyvinylamides for the purpose are known, some of which are commercially available.

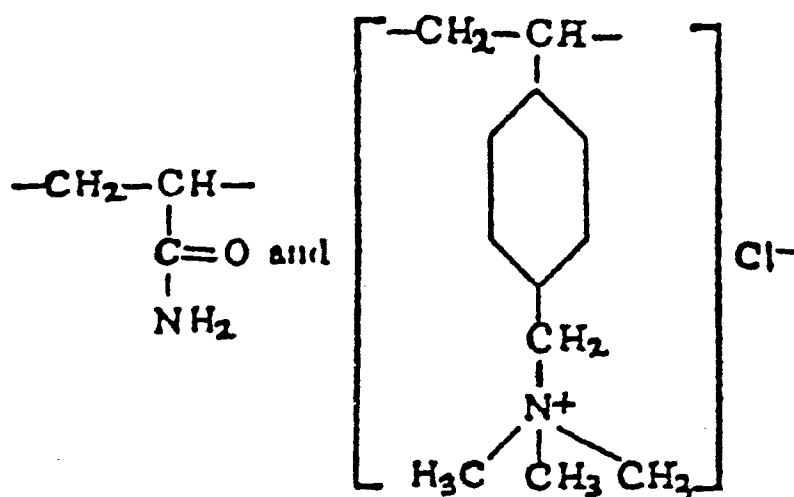
Cationic polyvinylamides suitable for reaction with glyoxal to form polymers of the present invention include those which are produced by copolymerizing a water-soluble vinylamide with a vinyl water-soluble monomer

which carries a positive electrostatic charge when dissolved in water, for example, 2-vinylpyridine, 2-vinyl-N-methylpyridinium chloride, diallyldimethyl ammonium chloride, (p-vinylphenyl)-trimethyl ammonium chloride,
 5 and 2-(dimethylamino) ethyl acrylate. Taking the latter compound as an example, the product polymer contains cationic



10 linkages. If desired, some or all of the tertiary nitrogen atoms therein can be quaternized, e.g., by reaction with dimethyl sulfate.

20 Alternatively, cationic polymers may be produced from non-ionic polyvinylamides, by converting part of the amide substituents thereof (which are non-ionic) to cationic substituents. One such polymer can be produced by treating polyacrylamide with an alkali metal hypohalite; part
 25 of the amide substituents are degraded by the Hofmann reaction to cationic amine substituents. For details of this procedure see House et al. U.S. Patent No. 2,729,560, which also discloses a number of other polyvinylamides which can be employed in place of polyacrylamide. An-
 30 other example is the 90:10 molar ratio acrylamide:p-chloromethylstyrene copolymer which is converted to cationic state by quaternization of the chloromethyl substituents with trimethylamine. The trimethylamine can be replaced in part or in whole with triethanolamine or other water-soluble tertiary amine. The resulting polymer is composed of linkages having the theoretical formulae:

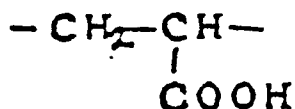


Alternatively still, cationic polymers can be prepared by polymerizing a water-soluble vinyl tertiary amine (for example, dimethylaminoethyl acrylate or vinylpyridine) with a water-soluble vinyl monomer copolymerizable therewith (for example, acrylamide) thereby forming a water-soluble cationic polymer. The tertiary amine groups can then be converted into quaternary ammonium groups by reaction with methyl chloride, dimethyl sulfate, benzyl chloride, etc. in known manner, with enhancement of the cationic properties of the polymer. Moreover, polyacrylamide can be rendered cationic by reaction with a small amount of glycidyl dimethyl ammonium chloride.

Anionic polymers of the present invention can be prepared as follows.

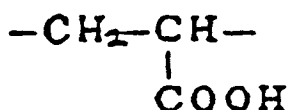
According to one method, a water-soluble aldehyde-reactive vinylamide (for example acrylamide and crotonamide) is copolymerized with a water-soluble vinyl acidic material, for example, acrylic acid, methacrylic acid, maleic acid, and vinylbenzenesulfonic acid, and the copolymer is reacted with glyoxal. The resulting polymer is anionic and thermosetting.

According to another method, the anionic substituents are formed in situ in the polymer. Thus in one embodiment of this method polyacrylamide is subjected to partial hydrolysis, resulting in formation of a vinyl polymer which comprises



5 linkages, or an alkali metal salt thereof. Moreover, ethyl acrylate is copolymerized with a suitable aldehyde-reactive compound (for example acrylamide), and the resulting polymer is subjected to hydrolysis. The product contains (—CH₂CHCONH₂—) and

10



15 linkages, and is reacted with glyoxal to form a thermosetting polymer.

According to a third method, a non-ionic hydrophilic thermosetting polyacrylamide-glyoxal polymer is reacted with sodium or potassium bisulfite, which introduces —SO₃K or —SO₃Na substituents into the polymer thereby rendering it anionic.

20

The aforementioned copolymerizations may be performed by any convenient method for the copolymerization of water-soluble monomers.

25

The reaction of the parent polymer with glyoxal is conveniently performed by warming a dilute neutral or slightly alkaline aqueous solution of glyoxal and an ionic vinylamide polymer until a slight increase in viscosity is observed. The solution then contains a polymer according to the present invention and is ready for use. If desired, the solution can be cooled to room temperature and acidified; the resulting solution possesses good stability.

30

The glyoxal reaction described above does not go to completion. For example, when a dilute aqueous solution of 25 mols of glyoxal and a 95:5 molar ratio acrylamide:diallyldimethyl ammonium chloride copolymer is

warmed until a slight increase in viscosity occurs, about half of the glyoxal (as determined by dialysis) does not react at all but remains dissolved in the water. Of the remaining glyoxal, the largest part reacts to the extent of only one of its functionalities (so as to introduce —CHOHCHO substituents into the polymer). The remainder of the glyoxal (a very small amount) reacts to the extent of both its functionalities (so as to unite two polymeric molecules) causing the slight increase in viscosity referred to above.

The glyoxal which does not react at all remains in the white water during the papermaking operation and does not act as a wet-strengthening agent.

The minimum amount of glyoxal in the starting solution is such that the polymer product is thermosetting according to the test set forth above. A larger amount of glyoxal may be employed, but the increase in wet strength produced by such larger amount is minor.

In most instances the amount of glyoxal taken, and the duration of the time allowed the polyvinylamide to react with the glyoxal, should be such that the molar ratio of —CHOHCHO substituents to the glyoxal-reactive amide substituents in the polymer is at least 0.06:1. This is about the minimum proportion of active glyoxal substituents needed to produce practically useful wet strength efficiency. The ratio may be higher, and a ratio in the range of 0.10–0.20 appears to afford best wet strength efficiency.

The optimum amount of glyoxal to be taken in any instance is readily found by laboratory trial using the examples which follow as guides. As a starting point in most instances, one mol of glyoxal may be taken for every four vinylamide units present.

The compositions of the present invention are conveniently employed in the manufacture of paper at polymer (solids) concentrations on the order of from about 1% to about 10%, based on the weight of the solution. The solutions can be usefully applied to preformed paper by the "tub" or impregnation method, but more conveniently are applied by adding the solutions directly to papermaking fibrous suspensions at any point in the papermaking system where wet-strength resins are customarily added. Alternatively, as mentioned, the compositions can be sprayed onto the final paper product.

The cationic polymers of the present invention are rapidly and substantively absorbed by the fibers at pH values within the range 3.5-8, and the use of retention aids is unnecessary. While best wet strength is achieved at low pH, very satisfactory wet strength is achieved with neutral pulps.

A substantial amount of wet strength is imparted when the amount of polymer adsorbed by the fibers is as little as 0.2% of the dry weight of the fibers, and evidently smaller amounts impart a significant amount of wet strength as well. The strengthening effect of the polymer increases over a broad range, up to at least 2% of the dry weight of the fibers.

The plateau range (the range over which amounts of polymer added to an aqueous suspension of cellulose paper-making fibers at a given pH produces negligible increases in wet strength) has not yet been ascertained for all fibers, but can be readily found by trial.

The anionic polymers are conveniently added in the same manner and in the same amount as the cationic agents, except that the use of retention agent is usually necessary. One suitable retention agent is alum, and this may be added in an effective amount prior to addition of the anionic polymer. If preferred, the alum may be added subsequent to addition of the polymer. In place of the alum there may be employed any of the known

5 cationic retention aids, for example, the melamine-formaldehyde acid colloid of U.S. Pat. No. 2,345,543, the adipic acid-diethylenetriamine-epichlorohydrin resin of U.S. Pat. No. 2,926,154; polyethylenimine, and polyvinylpyridine quaternized with butyl bromide. When alum is used as the retention aid, the optimum pH of the suspension for adsorption of the polymer and for rapid development of its wet-strength properties is about 4-5.5.

10 The mechanism by which the polymer of the present invention produces excellent temporary wet-strength has not been ascertained, and we do not wish to be bound by any theory. However, our evidence indicates that the polymer produces its strengthening action by two different reactions: a
15 chemical reaction with the cellulose, and a cross-linking reaction with itself.

The invention is described more in detail in the examples which follow. These examples constitute specific embodiments of the invention and are not to be construed as
20 limitations thereon.

The following Examples 1-10 illustrate the preparation and properties as polymer component of the temporary wet strength composition of the invention of a number of ionic, hydrophilic vinylamide polymers carrying a sufficient number of -CHOHCHO substituents to be thermosetting.
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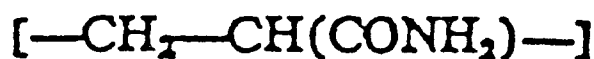
EXAMPLE 1

30 Acrylamide-diallyldimethyl ammonium chloride copolymer (97.8 mol percent acrylamide), glyoxal reacted

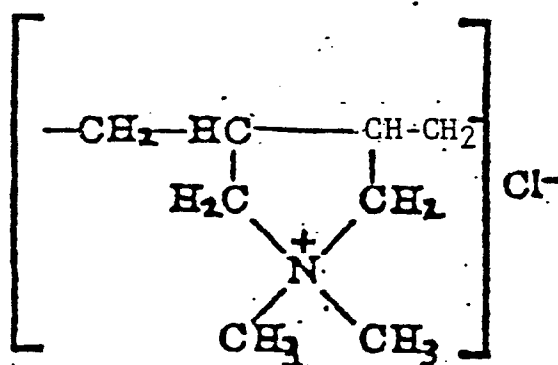
Into a reaction vessel equipped with reflux condenser, dropping funnel, stirrer and thermometer are placed 75.5 g. of water, 34.0 g. of isopropyl alcohol, and a solution of 4.0 g. of diallyldimethyl ammonium chloride in 4.3 g. of water. To these materials at reflux are slowly added 80.8 g. (1.15 mol) of acrylamide dissolved in 83.4 g. of water and 0.4 g. of ammonium persulfate dissolved in 16.2 g. of

water. The acrylamide: diallyldimethyl ammonium molar ratio is 97.8:2:2. Addition is complete in 100 minutes. The reaction mixture is refluxed for an additional two hours and is then cooled.

The product is a substantially linear non-thermosetting cationic polyacrylamide having a molecular weight in the range of 7,000-20,000 and is substantially composed of linkages having the theoretical formulae:



and



This polymer dissolves easily in water, forming a clear solution.

The solution is adjusted to pH 7.5 by addition of dilute sodium hydroxide or sulfuric acid, as required. There is then added sodium phosphate as buffer, followed by 42.0 g. of a 40% by weight solution of glyoxal in water. The solution is adjusted to 11% polymer solids by addition of water. The pH of the solution is adjusted to 8 and the pH is lowered to 7 as soon as a perceptible increase (i.e., an increase of 1 poise) occurs in the viscosity of the solution. The pH of the solution is then gradually lowered to keep the reaction progressing at a steady, moderate rate. When the polymer solution reaches a Gardner-Holdt viscosity of B-C as an 11% by weight solution at 30° C., the reaction is stopped by diluting the solution to 8% polymer solids,

adjusting the pH of the solution to 3.5, and cooling the solution to room temperature.

5 Dialysis of a sample of the solution shows that only about half of the glyoxal reacts with the polyacrylamide. Of this, only a small amount reacts bifunctionally (i.e., as cross-linking agent) with the polyacrylamide; this is the cause of the small increase in viscosity noted above. The remainder of the glyoxal reacts monofunctionally (i.e., so as to form —CHOHCHO substituents on the polymer, probably attached to the amide groups thereof). The resulting polymer is cationic and water-soluble. In the solution, the weight of wholly unreacted glyoxal is about $\frac{1}{12}$ of the weight of the polymer. The ratio of the glyoxal substituent on the backbone to the amide substituent is about 0.12:1.

10 The thermosetting nature of the polymer is shown by coating a glass panel with an 11% by weight aqueous solution of the polymer, air-drying the panel, and baking the panel for 5 minutes at 90°C . The resulting film does not dissolve in water at pH 7 and 20°C .

20 Similar results are obtained when the molar ratio of the acrylamide to the diallyl dimethyl ammonium chloride is in the range of 99:1 to 75:25.

25 On standing the solution remains clear. Initially, samples which are removed and diluted to 2%–5% solids. However, as the aging progresses, the samples which are removed and which are diluted to 2%–5% yield hazy solutions, which show that the polymer therein is in colloidal state.

30 The polymer is substantially uncolored as prepared. It does not darken or acquire a color as it ages.

Paper made with a temporary wet strength composition containing such polymer is unusually bright compared to other wet strength papers, due to the absence of color in the polymer and the low capability of the polymer to attract into the paper iron, dirt, etc., from the white water.

EXAMPLE 2

5 Acrylamide-acrylonitrile-diallyldimethyl ammonium chloride copolymer (75 mol percent acrylamide), glyoxal reacted

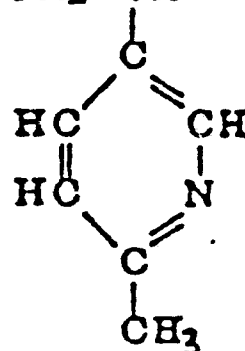
10 The procedure of Example 1 is repeated, except that 20.2 g. of the acrylamide is replaced by 15.1 g. of acrylonitrile and the amount of the glyoxal solution which is added is increased to 48.3 g. The acrylamide:acrylonitrile:diallyldimethyl ammonium chloride molar ratio is 75:25:2, and the ratio of the —CHOHCHO substituents to the amide substituents of the copolymer is approximately 0.17:1.

15 The initial copolymer is formed of linkages having the theoretical formulae shown in Example 1, plus the linkage having the theoretical formula $\text{—CH}_2\text{—CH(CN)—}$. Solutions of the polymer, as prepared, are usually hazy.

EXAMPLE 3

20 Methacrylamide-methylvinylpyridine copolymer (96.7 mol percent methacrylamide), glyoxal reacted

25 Into the reaction vessel of Example 1 are placed 75 g. of water and 35 g. of isopropyl alcohol, and the mixture is heated to reflux. To this solution there are added separately but concurrently over 1.5 hours 4.0 g. of 2-methyl-5-vinyl pyridine and 85 g. of methacrylamide dissolved in 105 g. of water containing 0.5 g. of ammonium persulfate. The polymer is composed of linkages having
30 the theoretical formulae



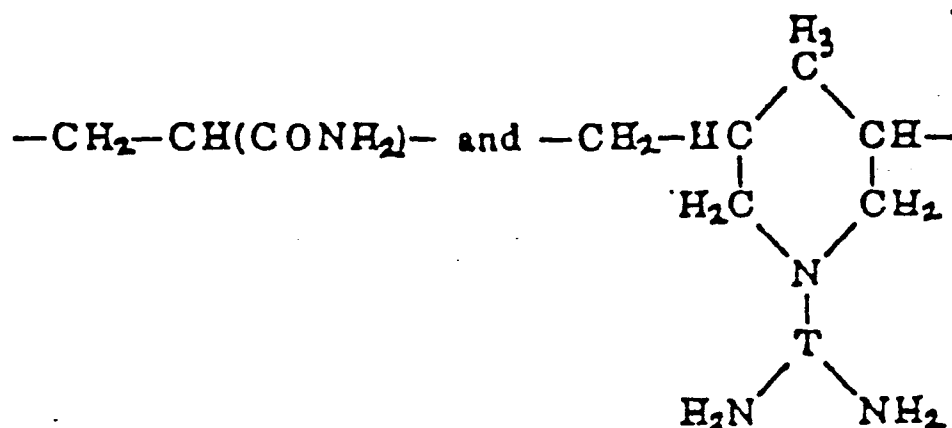
The product is diluted to 11% solids by weight, and adjusted to pH 7.5 with addition of buffer. There is then added 36.4 g. of 40% aqueous glyoxal solution, and the glyoxal is partially reacted with the polymer, all according to the method of Example 1. A thermosetting cationic water-soluble polymer is obtained, which is stabilized by acidification, cooling and dilution to 8% solids. The ratio of $-\text{CHOHCHO}$ substituents to the amide substituents is in excess of 0.06:1.

EXAMPLE 4

Acrylamide-diallylmelamine copolymer (90 mol percent acrylamide), glyoxal reacted

Into a flask provided with agitation, reflux condenser and electric heating mantle is placed 20.6 g. (0.1 mol) of diallylmelamine dissolved in dioxane, and to this is slowly added separately and concurrently a solution of 71 g. (1 mol) of acrylamide in dioxane and 0.5 g. of benzoyl peroxide dissolved in dioxane. The mixture is heated to 88° C. and cooling is applied to maintain the exotherm at 90° C. When the exotherm subsides, the flask is maintained at 100° C. for 90 minutes. The polymer is filtered off and is washed with dioxane; cf. U.S. Patent No. 3,077,430.

The copolymer is substantially composed of linkages having the theoretical formulae



wherein T designates the triazine ring of melamine.

The copolymer is dissolved in water and the solution adjusted to 11% solids by addition of water. The solution is adjusted to pH 7.5. Sodium phosphate buffer and 43 g. of 40% aqueous glyoxal solution are added. The mixture is further processed by the method of Example 1. A polymer having similar properties is obtained.

EXAMPLE 5

Poly(vinylurea), glyoxal reacted

To a solution of 43 g. (1 mol) of polyvinylamine in 100 cc. of water is added 83 ml. of 12 N hydrochloric acid (1 mol), after which 81 g. (1 mol) of potassium cyanate is added. The mixture is reacted at 75° C. for 1 hour with slow agitation. The product is poly(vinylurea), substantially composed of linkages having the theoretical formulae $\text{—CH}_2\text{CH(NHCONH}_2\text{)—}$, and perhaps some few unaltered $\text{—CH}_2\text{CH(NH}_2\text{)—}$ groups.

The syrup is diluted to 11% solids by addition of water and is adjusted to pH 7.5. Sodium phosphate buffer and 36 g. of a 40% solution of glyoxal in water are added.

Processing is continued by the method of Example 1. A similar polymer containing

5 -CHOHCHO

substituents is obtained.

EXAMPLE 6

Acrylamide - acrylic acid copolymer (92 mol percent
acrylamide), glyoxal reacted

10 The procedure of Example 1 is followed, except that the monomers employed are 92 g. of acrylamide and 8 g. of acrylic acid, the two monomers are premixed with the water, and this solution and the catalyst solution are added concurrently to the refluxing aqueous isopropanol. The
15 copolymer [composed of $-\text{CH}_2\text{CH}(\text{CONH}_2)-$ and $-\text{CH}_2\text{CH}(\text{COOH})-$ linkages] is reacted with glyoxal as shown in Example 1. A water-soluble thermosetting anionic polymer containing $-\text{CH}_2\text{CH}(\text{CONHCHOHCHO})$ linkages is obtained. The ratio of the $-\text{CHOHCHO}$ substituents to the amide substituents present in
20 the product is about 0.12:1. An aqueous solution of the product is initially clear, but becomes hazy on standing at room or elevated temperature of 2%-5% solids.

EXAMPLE 7

25 Polyacrylamide-glyoxal resin, sodium bisulfite reacted

To a solution of 71 g. (1 mol) of polyacrylamide (molecular weight 10,000) in water at pH 7.5 is added
30 a neutral buffer and then 36.6 g. (0.25 mol) of a 40% by weight solution of glyoxal in water. The solution is treated as shown in Example 1 to cause partial reaction of the glyoxal. The solution is adjusted to pH 4.5 with hydrochloric acid and to it is added 8.5 g. of sodium bisulfite. The pH of the solution is then readjusted to 4.5 with hydrochloric acid.

A water-soluble anionic thermosetting polymer is obtained substantially composed of linkages having the theoretical formulae $\text{—CH}_2\text{CH(CONH}_2\text{)—}$,



and $\text{—CH}_2\text{—CH(CONHCHOHCHOHSO}_3\text{Na)—}$. The ratio of —CHOHCHO to amide substituents in the product is about 0.12:1.

EXAMPLE 8

Polyacrylamide-3-(dimethylamino)propylamine-glyoxal copolymer

To 71 g. (1 mol) of polyacrylamide (molecular weight 10,000) dissolved in 200 g. of ethylene glyoxal is added 20 g. (0.2 mol) of 3-(dimethylamino)propylamine and the mixture is heated in a flask provided with an ammonia outlet and trap at 110° C. until 0.2 mol of NH_3 is evolved. The polymer is recovered by precipitation of the polymer from two liters of isopropyl alcohol. The polymer (87 g.) is dissolved in water and is reacted with 36.6 g. of 40% aqueous glyoxal (0.25 mol) by the method of Example 1.

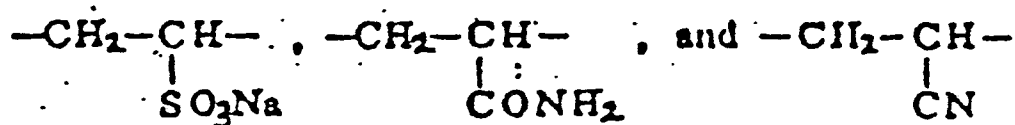
The product is a water-soluble thermosetting cationic polymer. The initial aqueous solution of the product is clear, and develops a colloidal haze on standing at room temperature and 2%–5% solids.

EXAMPLE 9

Vinylsulfonic acid-acrylamide-acrylonitrile copolymer, glyoxal reacted

Into a closed reactor containing a stirrer, thermometer, nitrogen gas inlet tube and dropping funnel are introduced (by the method of U.S. Patent No. 3,164,574) 20 g. of a 50% by weight aqueous solution of sodium vinylsul-

fonate, 1 g. of potassium persulfate, and 0.5 g. of $\text{Na}_2\text{S}_2\text{O}_5$, all air being swept from the reactor by a stream of nitrogen gas. The mixture is heated to 40°C . with stirring. There are then added dropwise over two hours a solution of 40 g. of sodium vinylsulfonate solution in 40 g. of water at pH 4.5 and a solution of 40 g. of acrylamide plus 10 g. of acrylonitrile in 100 g. of water. There is then added dropwise over $\frac{1}{2}$ hour 50 g. of water containing 0.5 g. of potassium persulfate and 0.25 g. of $\text{Na}_2\text{S}_2\text{O}_5$. Stirring is continued for 7 hours at 80°C . The polymer is precipitated by addition of methanol, and the precipitate is washed with methanol and dried. The polymer is substantially composed of linkages having the theoretical formulae.



71 g. of the polymer is dissolved in 630 g. of water. The solution is adjusted to pH 7.5 by addition of sodium hydroxide and buffer, and 36.0 g. of a 40% aqueous solution of glyoxal is added. Partial reaction between the polymer and the glyoxal is effected as shown in Example 1.

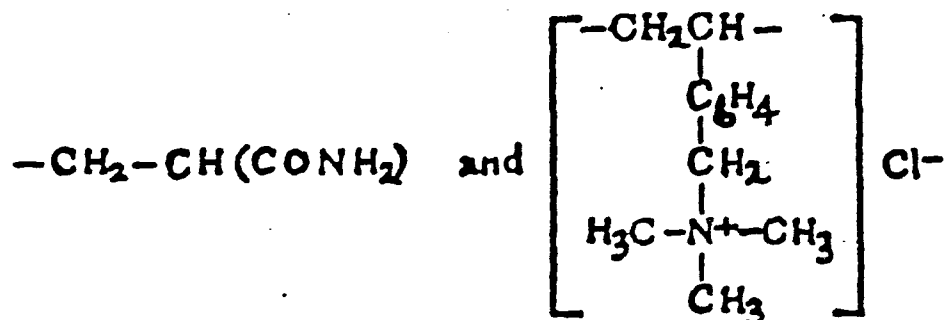
A water-soluble anionic thermosetting polymer containing ---CHOHCHO substituents is obtained. Dilute solutions of this polymer are often hazy as prepared.

EXAMPLE 10

Acrylamide-(p-vinylphenyl)trimethyl ammonium chloride copolymer, glyoxal reacted

32 g. (0.45 mol) of acrylamide and 7.6 g. (0.05 mol) of p-(chloromethyl) styrene are brought to reflux in 200 g. of acetone and 1.45 g. of benzoyl peroxide are added. After 3 hours of refluxing, the precipitated poly-

mer is collected and air-dried. To 50 g. of a 10% by weight solution of the polymer in water is added 7.0 g. of 40% aqueous trimethylamine. After the initial exotherm the solution is warmed at 40° C. until the pH falls below 7.0. The resulting polymer is substantially composed of linkages having the theoretical formulae



The solution is diluted to 100 ml. with water and to it is added 15.0 g. of 40% aqueous glyoxal solution. The pH is adjusted to 8.0 with sodium carbonate and the glyoxal is partially reacted with the polymer according to the method of Example 1.

A water-soluble cationic thermosetting polymer containing $-\text{CHOHCHO}$ substituents is obtained, which becomes hazy on standing at 2%–5% solids.

EXAMPLE 11

The following illustrates a preferred method for manufacturing wet-strength paper according to the present invention.

- 25 -

An aqueous solution was prepared containing one percent by weight, based on the weight of solution, of the vinylamide polymer of Example 1. This solution was divided into two aliquots, one of which (Sample A) was used in the subsequent procedure as described hereinafter without further modification, while the other aliquot (Sample B) was modified by addition thereto of sufficient quantity of 1.9 N sodium hydroxide solution to raise the pH level thereof to approximately 9.6. A two percent by weight solution of the vinylamide polymer of Example 1 also was prepared and likewise treated by addition of sufficient quantity of 1.9 N sodium hydroxide solution to raise the pH level thereof to approximately 9.6 (Sample C). Samples B and C then were "aged" by allowing same to react overnight for 15-16 hours. It is to be noted here that the subsequent reaction occurring after adjustment of the pH of the vinylamide polymer-containing solution of the present invention to a value of about 9 to about 11 will result in diminution of the pH to values which may for example be on the order of about 7 to about 8. As referred to herein, however, the pH which is identified in connection with the addition of strong base to the vinylamide polymer-containing solution is the initial pH to which the solution is adjusted in the range of from about 9 to about 11 and not the lower value which results from the completion of reaction over an extended period of time.

Also included in the evaluation for comparison purposes was a quantity of dialdehyde starch (DAS), which is commercially known for impartation of temporary wet strength to paper (Sample D).

A 0.6 percent by weight slurry of cellulosic fibers then was prepared as a furnish for making of paper on a stationary deckle Noble and Wood papermaking machine, to produce eight inch x eight inch seventy pound basis weight handsheets. The water employed to make the furnish was at a pH of 6.5 and contained 200 parts per million (ppm) sulfate anion and 50 ppm calcium ion.

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In separate runs, Samples A-D were respectively added to the furnish at a dosage level of 15 pounds vinylamide polymer per ton of furnish for Samples A-C and at a concentration of 15 pounds starch per ton for Sample D.

5 Immediately after its formation, the paper product in each run was subjected to determination of wet strength on a Twing-Albert tensile tester. The immediate or "on machine" wet strength value was determined by wetting a strip of sample paper one half inch wide and three
10 inches long while the strip of paper is mounted on the tensile tester and immediately recording the breaking wet strength. The wetting medium employed is deionized water buffered at a pH of 6.86.

15 Corresponding dry strength measurements were made on the tensile tester of dry strips of the product paper, which in all cases were cut from the product handsheets.

Wet tensile strength measurements were made after a 30 minute soak in water of a composition containing 6 ppm Mg^{++} , 140 ppm $CaCl_2$, 500 ppm bicarbonate and 85 ppm sulfate
20 anion concentrations, adjusted to a pH of 7.8. The 30 minute soak wet strength values were recorded and the percent decay in wet strength over the 30 minute soak period was determined as follows:

25

$$\begin{array}{l} \% \text{ decay after} \\ 30 \text{ minute soak} \end{array} = \left[\frac{(\text{wet strength after 30 minute soak}) - (\text{immediate wet strength})}{\text{immediate wet strength}} \right] \times 100$$

30 The wet and dry strength values and the 30 minute percentage decay are set out in Table I below for each of the runs with Samples A-D.

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TABLE I

SAMPLE	IMMEDIATE WET STRENGTH POUNDS PER INCH	DRY STRENGTH, POUNDS PER INCH	WET STRENGTH AFTER 30 MINUTE SOAK	WET TO DRY STRENGTH RATIO, PERCENT	WET STRENGTH 30 MINUTE DECAY, %
A	5.40	30.14	2.82	17.9	47.7
B	4.07	29.39	1.51	13.8	62.9
C	4.03	30.90	1.56	13.0	61.3
D	3.19	26.20	1.25	12.2	60.8

The results shown in the foregoing table indicate that the composition of the invention (Samples B and C) provide 30 minute decay of wet strength which exceeds that achievable with the commercially known dialdehyde starch (Sample D) which although effective is quite expensive and thus has not enjoyed widespread commercial usage. In addition the data show that the pH elevation treatment of the vinylamide polymer aqueous solution with a strong base substantially improves the decay of wet strength in a substantially neutral aqueous medium (pH of 6.5), relative to the prior art wet strength composition lacking such strong base treatment and pH adjustment.

Example 12

In this experiment, an aqueous solution of the polymer of Example I was made up at one percent solids, in accordance with the procedure set forth for the making of Sample B and six aliquots thereof (Samples F-K) were adjusted by addition thereto of sodium hydroxide to various respective pH levels as identified in Table II below. Also tested was an aqueous solution of the vinylamide polymer at one percent solids, but without base treatment/pH adjustment (Sample E having a pH of 3.5).

Samples F-K after pH adjustment by base addition were reacted at room temperature overnight (20 hours). Following overnight reaction, the Samples F-K were stabilized by addition thereto of sufficient quantity of hydrochloric acid to adjust the pH thereof to a value of 3.5.

Immediate wet strength and 30 minute soak wet strength values then were determined for each of the Samples E-K, and the 30 minute decay values (percent) were calculated, as set forth in Table II below.

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Table II

	<u>Sample</u>	<u>Base-Adjusted pH</u>	<u>Decay in Wet Strength After 30 Minute Soak,</u>
	E	unadjusted	45.8
5	F	7.5	52.0
	G	8.0	51.5
	H	8.5	57.0
10	I	9.0	60.8
	J	9.5	60.8
	K	10.0	61.0
15			
20			
25			
30			

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Inasmuch as the 30 minute decay values are indicative of the degradability of the paper in aqueous medium, with values on the order of 55-65 percent generally being desirable for paper products such as tissue and towel-
5 ling, it is apparent that Samples H-K prepared with adjustment of pH to values in the range of 8.5 to 10.0 by addition of strong base to the vinylamide polymer solution in accordance with the present invention, provide highly advantageous decay levels, whereas the unadjusted vinylamide polymer solu-
10 tion of Sample E (no strong base addition) and Samples F and G, wherein pH adjustment by strong base addition was to levels of 7.5 and 8.0 respectively, exhibit markedly inferior performance relative to the compositions of the present invention.

15 Example 13

Another experiment was conducted to evaluate the effect of the concentration of vinylamide polymer in the aqueous temporary wet strength composition. Aqueous compositions containing one percent by weight of vinylamide
20 polymer were prepared in accordance with the procedure set for in Example 11 (Samples L and M). A corresponding sample of the vinylamide polymer of Example 1 was prepared at a solids concentration of three percent by weight (Sample N). Each of Samples L and M were adjusted by strong base
25 addition to a pH of 9.5; Sample N was adjusted by base addition to pH of 9.8. Each of these samples after reaction for 16 hours was stabilized by addition of hydrochloric acid thereto to adjust the pH to a value of 3.5. For comparison purposes, dialdehyde starch, (Sample O) and the
30 vinylamide polymer unadjusted by base addition (Sample P) were included 30 minute soak decay in wet strength was then determined as in the preceding example. The results are set forth below in Table III.

Table III

	<u>Sample</u>	<u>Decay in Wet Strength After 30 Minute Soak, %</u>
	L	67.0
5	M	69.0
	N	62.0
	O	67.5
	P	52.7
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15		
20		
25		
30		

Example 14

In this experiment, an aqueous solution containing five percent by weight of the vinylamide polymer of Example 1 was prepared. The solution was adjusted to a pH of 8.5 by addition thereto of 1.9N sodium hydroxide and thereafter was reacted in a constant temperature water bath at a temperature of 75°C.

The (reacted) solution was stabilized by addition thereto of sufficient quantity of hydrochloric acid to adjust its pH to 3.5. This solution (Sample 12) was evaluated for imparting temporary wet strength to paper by the procedure of Example 11, against a dialdehyde starch control (Sample R). Results are shown below.

15

Table IV

<u>Sample</u>	<u>Decay in Wet Strength After 30 Minute Soak, %</u>
Q	57.3
R	63.2

20

These data show that the composition according to the present invention provides high levels of wet strength decay, on the order of that achieved by the dialdehyde starch control.

25

Example 15

Another experiment was conducted to evaluate the effect of hydroxy-containing solvents on preparing higher solids vinylamide polymers for temporary wet strength. An aqueous composition containing 15 percent by weight propylene glycol and 5% by weight of the vinylamide polymer of Example 1 was prepared in accordance with the procedure set forth in Example 11 (Sample S). A corresponding sample of the vinylamide polymer of Example 1 was prepared at a solids concentration of one percent by weight (Sample T).

Sample S was adjusted by strong base addition to a pH of 9.0. This sample was reacted for 36 hours and stabilized with acid to a pH of 3.5. For comparison purposes, dialdehyde starch (Sample U) and the vinylamide polymer

unadjusted by base addition (Sample V) were included in the 30 minute soak test. The results are shown in Table V.

Table V

<u>Sample</u>	<u>Decay in Wet Strength After 30 Minute Soak, %</u>
S	60.2
T	68.4
U	59.9
V	40.9

Example 16

An aqueous solution containing five percent by weight of the vinylamide polymer of Example 1 was prepared. The solution was buffered by addition thereto of monobasic phosphate and placed in a constant temperature ice bath at 11°C with the pH of the solution being adjusted to 9.5 by addition of 1.9N sodium hydroxide. Paper treated with this solution was tested for dry and wet strength characterized by the procedure of Example 11. Such paper exhibited a dry tensile strength of 24.64 lbs. per inch, an immediate wet strength of 3.84 lbs. per inch, a 30 minute soak wet strength of 1.44 lbs. per inch. The wet-to-dry strength ratio of the paper was 15.58 and the decay in wet strength after the 30 minute soak was 62.5%.

Example 17

Aqueous solutions were made up of the vinylamide polymer of Example 1 at weight percent concentrations of 1% (Samples S and X) and 4% (Samples Y and Z), for comparison against a dialdehyde starch control (Sample AA). Sample W was not further treated by strong base addition in the manner of the present invention. Sample X was treated with sodium hydroxide to adjust the pH of the solution to 9.8, followed by acidification with hydrochloric

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acid to a pH of 3.5 for stabilization of the solution. Sample 4 contained 4.9% by weight vinylamide polymer in a solvent comprising 97.6% by weight water and 2.4% by weight methanol; this solution was adjusted by base addition to a pH of 10, reacted for four minutes and then acidified to a pH of 3.5. Sample Z contained 4% by weight vinylamide polymer in a solvent comprising 80% water and 20% methanol (by weight); the solution was basified to a pH of 10, reacted for 16 minutes and then acidified to a pH of 3.5.

Wet-to-dry strength ratios and 30 minute wet strength decay values were then determined for paper sheets treated with each of the samples. The resulting data are set forth below in Table IV.

Table IV

<u>Sample</u>	<u>Wet-to-Dry Strength Ratio, %</u>	<u>Wet Strength Decay After 30 Minute Soak, %</u>
W	17.4	47.7
X	11.5	66.3
Y	13.0	58.1
Z	10.6	63.6
AA	10.5	61.0

29,449 WHAT IS CLAIMED IS:

1. A composition for imparting temporary wet strength to paper, comprising a solution containing from about one percent to about ten percent by weight, based on the weight of said solution, of a water-soluble vinylamide polymer having sufficient glyoxal-reactive amide substituents and -CHOHCHO substituents to be thermosetting, in a solvent selected from the group consisting of water, water-miscible solvents containing free hydroxyl functionality, and mixtures thereof, the ratio of the number of said -CHOHCHO substituents to the number of said glyoxal-reactive amide substituents being in excess of 0.06:1, to which has been added a sufficient quantity of a strong base for reaction therewith to adjust the pH of the solution to a value of from about 8.5 to about 11.
2. A composition according to Claim 1, wherein the solution has been stabilized for enhancement of shelf life of said composition, by addition thereto of a sufficient quantity of a mineral acid to adjust the pH of said solution to a value of from about 3 to about 4.
3. A composition according to Claim 1, wherein said polymer is in colloidal state in said aqueous solution.
4. A composition according to Claim 1, wherein said solvent containing free hydroxyl functionality is selected from the group consisting of methanol, ethanol, ethylene glycol and propylene glycol.
5. A composition according to Claim 1, wherein said polymer is a cationic polymer.
6. A composition according to Claim 1, wherein said polymer is a cationic water-soluble about 99:1 to 75:25 molar ratio acrylamide:diallyldimethyl ammonium chloride polymer.
7. A composition according to Claim 1, wherein said pH is adjusted by addition of a strong base to a value in the range of from about 9.0 to about 10.6.
8. A composition according to Claim 2, wherein said aqueous solution is stabilized by addition of suffi-

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cient quantity of said mineral acid to adjust the pH thereof to a value of from about 3.2 to about 3.8.

9. A composition according to Claim 1 wherein said strong base is selected from the group consisting of potassium hydroxide and sodium hydroxide.

10. A composition according to Claim 1, wherein said strong base is sodium hydroxide.

11. A composition according to Claim 2, wherein said mineral acid is selected from the group consisting of hydrochloric acid, sulfuric acid and nitric acid.

12. A composition according to Claim 2 wherein said mineral acid is hydrochloric acid.

13. A process for imparting temporary wet strength to paper, comprising applying thereto a wet strengtheningly effective amount of the aqueous composition according to Claim 1.

14. A process according to Claim 13, wherein said aqueous composition is applied to said paper by spray application.

15. A process for imparting temporary wet strength to paper manufactured from an aqueous suspension of cellulose paper-making fibers, comprising adding to said aqueous suspension a wet strengtheningly effective amount of the aqueous composition according to Claim 1.

16. Paper with temporary wet strength, having applied thereto a wet strengtheningly effective amount of the aqueous composition of Claim 1.