ACROLEIN-N-VINYL PYRROLIDONE COPOLYMER AND CATIONIC DERIVATIVES PAPER WET-STRENGTH AGENTS

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ABSTRACT OF THE DISCLOSURE

This invention relates to novel wet strength agents comprising water-soluble copolymers of monomers such as acrolein and n-vinyl pyrrolidone prepared by carrying out the polymerization as a dilute aqueous reaction mixture containing below about 10% of the monomers during at least one-third the period of polymerization. Also, the invention relates to cationic forms of these copolymers which have been so made cationic by reaction with an amine reactant. A specific method as set out above is also disclosed.

THE DISCLOSURE


It is known that the majority of papers produced without benefit of specific additives when subjected to water or even a moist environment have an extremely low wet strength and easily disintegrate or tear upon handling of any severity.

It has been theorized that the low strength of wet papers is the result of a softening of the fibers and consequent reduction of the bond between them. The wetted papers have approximately only 5—10% of the strength possessed when dry. It is generally thought that in the contacting fibers in a dry sheet of paper there is some small portion of a cellulosic structure held commonly by the fibers. This cellulosic structure is considered hydrophilic or capable of intimate association with water, though not actually soluble therein. The cohesive strength which normally exists when the paper is in the dry state is substantially reduced when contacted with water, whereby the bonding or adhesion effect between the cellulosic fibers is altered. Thus the cementation of fibers is destroyed and the paper as a whole loses its strength. The adhesion or bonding between the individual fibers in contact with each other, which has been developed upon drying the interleaved web from a suspension of water, is reduced to a point whereby the continuous sheet is virtually useless in certain functions involving contact with water.

Prior art attempts to obviate the above problem and measurably increase the wet strength of papers have generally met with success only through means of addition of certain chemical agents to the paper pulp suspension prior to formation of the wet sheet. However, while wet strengths of paper have been increased by such chemical treatment, other subsidiary problems arise with such treatment. For example, in many instances the increase in wet tensile strength property is concurrently accompanied by a corresponding decrease in desired high absorptive capacity. This loss of absorption is generally due to coating of the paper surface by the additive chemical. Yet, when paper is to be used for such purposes as toweling it is essential that both the desiderata of wet strength and absorptive capacity are present.

Many other problems arise when chemically treating paper pulp to measurably increase wet strength of products therefrom. For example, such treatment also has the effect of decreasing the flexibility of the paper product whereby it cannot be molded or shaped into the desired form. Such paper products are often extremely stiff or hard. Likewise, the treated paper often becomes brittle or abrasive and useless for certain roles such as for hand or face tissues. Other paper products, while having the desired tensile strength when wet, lack pliability or drapability. Thus, when such paper products are crushed or crumpled, permanent undesirable creases or wrinkles are formed.

In addition to the above problems created by certain chemical additives, there is a tendency for some additives to measurably decrease the porosity and permeability of the paper product to the point where it cannot "breathe." Again such characteristic is undesirable in many areas of use.

Certain polymeric substances have been proposed and have found acceptance as wet strength additives. Again, these have certain drawbacks. For example, many further polymerize or react with the fibers of the paper pulp to an undesirable degree upon process heating of the pulp to form a sheet thereof. Thus, an excessive cure can cause many of the above discussed problems. Likewise, a serious problem exists with use of many polymers in that the requisite solubility or compatibility with the aqueous paper pulp is not present. For example, certain unsaturated aldehydes such as acrolein, when polymerized, form water-insoluble masses which can only be incorporated into the pulp after their chemical conversion by reaction with auxiliary chemicals such as sulfur dioxide or alkali metal bisulfites which impart an anionic character to the polymers. These reagents react with the aldehyde groups to form acetals and render the polymer molecules sufficiently soluble for use as wet strength agents. Also, in this regard use of anionic polymers as wet strength promoters generally requires further addition to the pulp of a retention aid such as alum. Without benefit of this auxiliary chemical only a portion of the polymer is retained on the paper sheet leading to inefficient promotion of wet strength.

Some effort has been made to overcome the necessity of making further derivatives of unsaturated polymers before they can be effectively used as paper additives. For example, U.S. Patent 2,657,192 affects the polymerization of acrolein in alcohol. Such a process has certain disadvantages in that it must be carried out in the more expensive organic solvents, and the resultant product is only soluble in such organic solvents. Also, since the reaction is carried out in the presence of alcohol there is a tendency to form acetals in situ, and thus lower the consequent molecular weight of the product. It is generally felt that for best effectiveness as a wet strength agent, a relatively high molecular weight polymer is generally needed.

It would therefore be of benefit to the art if paper wet strength additives could be produced whereby the tensile strength of the paper products is increased when wet without deleteriously affecting the other desirable properties of absorptive capacity, flexibility, pliability, porosity, etc. It would be of a further advantage to the art if water-soluble polymers of unsaturated aldehydes could be synthesized in a one-step process without resort to subsequent derivative modifications. If such aldehyde
polymers could be produced which have the requisite water-solubility for direct incorporation into an aqueous paper pulp system, and yet have relatively high molecular weights, thereby giving effective wet strength character to the products would find acceptance in the art. Again, if such additives had the effect of imparting wet strength character to paper products even when added to the precursor pulp in relatively small amounts, polymeric substances of this type would be extremely useful. Lastly, if these effective wet strength agents for a wide variety of paper stocks, a substantial improvement in the art would be realized. It therefore becomes an object of the invention to provide chemical compositions useful as paper wet strength additives.

Another object of the invention is to provide a method of greatly increasing the tensile strength of paper products when wetted and to furnish paper articles which concurrently possess other necessary characteristics of flexibility, water absorbency, porosity, drapability, etc.

Yet another object of the invention is to provide interpolymermers from unsaturated acrolein monomers, which have no anionic substituents and which may be used directly as water-soluble reaction products. A specific object of the invention is to provide copolymers and terpolymers of unsaturated aldehydes which are sufficiently water-soluble so as to be directly incorporated into paper pulp slurries without further modification of structure. Special manipulative techniques are disclosed with respect to achieving these water-soluble polymeric species.

And still another object of the invention is to provide cationic derivatives of the above copolymers and terpolymers which are especially useful in treating specific types of paper stock.

A further object of the invention is to provide copolymers and terpolymers of alpha-beta unsaturated aldehyde monomers having no anionic substituents and which have the requisite water solubility, high molecular weight and effectiveness as a paper wet strength agent even at relatively low use concentrations and without the use of aluminum salts as a retention device.

Other objects will appear hereinafter.

In accordance with the invention, it has been discovered that a certain class of alpha-beta-unsaturated aldehyde monomers are extremely useful in imparting high wet strength to paper products so treated with these additives. In its broadest aspect the invention lies in the discovery of certain new copolymers, terpolymers and cationic derivatives thereof, their method of preparation and the process of employing same in the paper manufacturing art. The interpolymermers of the invention have no anionic substituents and contain at least the polymerized monomers of alpha-beta-unsaturated aldehydes and nitrogen heterocycles containing an ethynylidene unsaturated group capable of Interpolymerization with the above aldehydes. For the sake of simplicity and convenience, the polymers of the invention will be listed and discussed according to the various classes which have been synthesized.

WATER-SOLUBLE COPOLYMERS

The first class of useful polymeric wet strength additives of the invention are composed of water-soluble copolymers of an alpha-beta-unsaturated aldehyde and a nitrogen heterocycle containing an ethynylidene unsaturated group capable of copolymerization with such aldehydes. These copolymers, as will be discussed in more detail below, may be synthesized by various manipulative techniques so that they are soluble up to about 10% by weight in water or aqueous liquids containing a measurable portion of water. Further, these copolymers contain no anionic substituents. Such copolymers may then be used directly as aqueous reaction products or further diluted prior to actual incorporation with the paper pulp.

The aldehyde monomers useful in the invention may be represented by the general formula:

$$R_1 R_2 CH=\overset{\text{C}}{\text{C}} \overset{\text{I}}{\text{O}}$$

where $R_1$ and $R_2$ may be either hydrogen, lower alkyl radicals or halogen. When the backbone of the aldehyde molecule contains attached thereto an alkyl radical, it is preferred that these radicals contain less than 6 carbon atoms and more preferably 3 carbon atoms or less. Useful alpha-beta-unsaturated aldehydes may be chosen from among acrolein, alpha-methyl acrolein, alpha-ethyl acrolein, alpha-propyl acrolein, alpha-isobutyl acrolein, alpha-amy1 acrolein, alpha-n-hexyl acrolein, alpha-bromo acrolein, etc. Other representative aldehyde monomers are crotonaldehyde, alpha-chlorocrotonaldehyde, beta-chlorocrotonaldehyde, alpha-bromo-crotonaldehyde, alpha-beta-dichlorocrotonaldehyde, alpha-beta-dimethyl acrolein, alpha-methyl-beta-ethyl acrolein, alpha-methyl-beta-isopropyl acrolein, alpha-ethyl-beta-propyl acrolein, etc.

The other monomeric substance going to make up this class of copolymers comprises a nitrogen heterocycle having externally attached to the ring, or ethynylidene unsaturated group capable of copolymerization with the above type aldehydes. Such may be chosen from a wide variety of monomeric substances such as vinyl oxazolidones, vinyl imidazoles, vinyl imidazolines, vinyl pyridines, vinyl pyrroldiones such as $N$-vinyl pyrrolidone, $2\text{-vinyl pyrrolidone}$, etc. Other specific nitrogen heterocycles useful as monomeric starting reagents include $N$-vinyl-5-methyl-2-oxazolidone, $N$-vinyl-2-oxazolidone, $N$-vinyl imidazole, $N$-vinyl-2-methyl imidazole, $2\text{-vinyl imidazole}$ $N$-vinyl-3 - morpholinone, $N$-vinyl caprolactam, etc. Preferred among these nitrogen heterocycles are the vinyl pyrroldiones. Excellent wet strength additives have been made in which the starting monomer mixture contains from 10 to 80 mole percent acrolein monomer and 20 to 90 mole percent nitrogen monomer. Preferred mixtures contain 20 to 67 mole percent acrolein monomer and 33 to 80 mole percent nitrogen monomer.

The comonomers may be polymerized by a wide variety of synthetic techniques including bulk, solution, emulsion, suspension, etc., polymerizations. One preferred method is polymerization by emulsion techniques. In its broadest aspect this procedure involves adding of the two monomers to an aqueous solution containing a catalyst and suitable amount of an emulsifying agent. Preferably, the reaction flask has been previously purged with an inert gas such as nitrogen. Almost any type of known emulsifier may be employed, but preferred are o xoalkylated alkyl phenols, such as the well-known "Triton" materials, ethylene oxide condensates of fatty acid amides such as "Ethomides-15, O-15 and HT-15," as well as "Aralco 80" and "Span," which are sorbitan monoolesates. Other suitable emulsifying agents are sorbitan mono esters, sodium dodecyl benzene sulfonate, aluminum stearates, aluminum oleates, etc. Only minute amounts of these emulsifiers are necessary, say from about 10 to about 1000 p.p.m. The concentration of the active monomer ingredients in the reaction mixture may be as low as about 1.0% and as highly concentrated as an emulsion containing 99.0% monomer subject to the last described dilution requirement. The reaction itself may be run in the presence of air, but it is preferred that the reaction vessel be first purged with an inert gas such at nitrogen, carbon dioxide, etc., in order to rid the system of oxygen having some part of a tendency to inhibit polymerization and provide lower product molecular weight.

The catalysts that are employed in the process include conventional peroxodic oxidizing agents such as potassium persulfate, hydrogen peroxide, and ammonium persulfate. It is preferred that water-soluble compounds be used for this purpose. The amount of catalyst used in the
process can vary from 0.003% to about 0.2% by weight based on the weight of the monomers. The preferred range is from about 0.05% to 0.1%. In a preferred embodiment, the polymerization action is carried out using a redox type catalytic system. In this method it is particularly preferred to remove oxygen from the system and introduce an inert gas therein in order to permit the catalyst to form free radicals. In a redox system, the catalyst is activated by means of reducing agent which, in the absence of oxygen, immediately produces free radicals without the use of heat. One of the reducing agents most commonly used is sodium metabisulfite. Other suitable agents include water-soluble thiosulfates, hydrosulfites, and reducing salts such as the sulfates of metals which are capable to existing in more than one valent state. The metals include cobalt, iron, nickel and copper. Another excellent reducing agent is silver nitrate. The use of a redox initiator system has several advantages, the most important of which is that it is possible to carry out the polymerization at lower temperatures since it is not required to decompose the catalyst. The catalyst and the active species may, if desired, be dissolved in a small amount of water and then added to the reaction mixture containing the emulsified monomers. Also, the catalyst initiator may be added directly to the emulsion and dissolved therein with mild agitation.

The polymerization itself is carried out at rather low temperatures, and preferably below about 80° C. More preferably, the reaction is carried out at a temperature range of 20–60° C, for a period of time of at least one hour. Excellent polymers have been formed in from about 1 to about 3 hours reaction time.

The water-soluble copolymers of the above discussed type were prepared by the simple expedient of effecting polymerization of the mixture of monomers while keeping the monomer solids content below about 10% by weight during at least ½ of the reaction time and more preferably between ⅓ and ⅔ of the time of reaction. Water-soluble copolymers having satisfactory wet strength activity are prepared by dilution below 10% concentration during the last ⅓ of the reaction period. It is believed that these are the first acrylon type interpolymers produced directly in a water-soluble state as reaction products without resort to subsequent modification such as sodium sulphite salts, sulphur dioxide, etc., and interpolymerization with monomers containing anionic groups such as anionic sulfur-containing comonomers.

As stated above, the concentration of monomers at the start of the reaction may be as high as 50%. But during the reaction itself, dilution with water must be effected so that the above requirement of dilution during reaction is met. This addition of water may be carried in a step-wise manner as by slug feeding or by continuous slow dripping into the reaction media. In any case, all that is essential is that during at least one-third of the reaction time, the concentration of reactants, existing in form of polymer and/or its parent unpolymerized monomer species, be kept below about 10% by weight solids content. Products synthesized by this method generally have solubility in water up to about 10% by weight.

If one desires that the water-soluble products be kept in an aqueous homogeneous condition for long periods of time, known stabilizers such as hydroquinones and other anti-oxidants may be added in small amounts to the final aqueous product. As little as 0.01% of stabilizer is effective. However, products having excellent long-term stability as homogeneous solutions in water, may be prepared without benefit of stabilizer.

The water-soluble acrylon derivatives prepared as outlined above show excellent activity as wet strength agents without benefit of any additional agent. Due to the fact that these polymers contain no anionic substituents, it is unnecessary to employ aluminum salts to aid in retention. It is believed that these are the first water-soluble acrylon type interpolymers which may be added to the paper pulp slurry without a retention aid such as alum or other aluminum salts and still achieve superior wet strength. It has been discovered that polymers containing even minor amounts of anionic groups or constituents require benefit of retention aids to be effective wet strength agents. The process of the invention is therefore a distinct advance in the art in that extremely efficient results may be obtained with sole use of the defined polymers which should be free of any anionic character.

CATIONIC WATER-SOLUBLE COPOLYMERS

These cationic derivatives are easily prepared by reacting any desired amount of water-soluble amine or amine quaternary with the above produced water-soluble copolymers. The cationic reaction is preferably run in about ½ hour to 2 hours at a temperature below 80° C. and more preferably between 10° and 60° C. These cationic copolymers show particular use in treating pulps which are anionic or neutral in character, such as highly bleached paper pulps. Again, excellent results are shown without the use of aluminum salt.

The amount of amine or amine quaternary reactant added to the water-soluble copolymer may vary considerably. More preferably, the mole ratio of water-soluble copolymer to the amine reactant ranges from 50:1 to 1:1. Most preferably, the mole ratio of copolymer to amine ranges from 25:1 to 5:1.

The amine modifier may be any molecule containing 2 or more amine groups either in the form of the free amine base and/or as quaternary groups. The amines themselves may be primary, secondary or tertiary. Thus, suitable modifiers may be ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine or partially or fully quarternized derivatives of any of the foregoing, hydrazines, hydrazides and quaternaries thereof such as betain-hydrazide chloride, N-N dimethyl-glycine hydrazide, unsymmetrical dimethyl hydrazides, polymers such as those formed by reaction of urea and polyamine polynamines, guanidines, biguanides, guanyl-urase, mono- and polyhydroxy polynamines and quaternaries thereof, etc.

WATER-SOLUBLE TERPOLYMERS

Other useful interpolymers of the acrylon type are terpolymers. These are made by polymerizing a mixture containing an alpha-beta-ethylenically unsaturated aldehyde monomer, a nitrogen heterocycle containing an ethylenically unsaturated group and an ethylenically unsaturated monomer containing a non-ionic hydrophilic radical as a side-chain. The first two monomer materials have been discussed in detail above, and need no further elaboration. The third monomer going to make up the useful terpolymers of the invention may be chosen from a wide variety of available materials, with the only requirement being that the monomer contain no anionic substituent. In each case the monomer contains an ethylenically unsaturated group in the backbone of the molecule and a non-ionic hydrophilic radical existing as a side-chain off the backbone.

Useful ethylenically unsaturated monomers containing a non-anionic, that is, a nonionic or cationic hydrophilic or water solubility promoting group, include those in which the hydrophilic group consists of amines class consisting of carboxylic acid amide, hydroxyl, hydroxyl alkyl ether, and the like. Specific monomers include hydroxyethyl acrylate or methacrylate, vinyl acetate, vinyl methyl ether, etc.

The water-soluble terpolymers are prepared in a manner like that used to make the copolymers whose mode of polymerization was described in detail above. Again, such reaction is carried out by maintaining the active solids concentration of the reactants below about 10% by weight during at least ⅓ of the reaction time. The polymerization is preferably carried out in aqueous media. It has been determined that for best results the
proportions of the respective three monomers employed, range in mol percents of from about 10 to about 70% of each monomer.

Likewise, cationic derivatives of the above type terpolymers may be easily prepared in the same manner as discussed above. The cationic derivatives of the water-soluble terpolymers are excellent wet strength agents used without additional salts. As in the case of the cationic copolymers, the cationically modified terpolymers find particular use in promoting the wet-strength of paper derived from alpha-sulfite pulps.

METHOD OF APPLICATION

The water-soluble copolymers, terpolymers and cationic derivatives thereof may be added to any type of paper in order to increase the wet-strength of the subsequently formed paper product. It is greatly preferred, however, that when anionic and non-ionic paper pulps are to be treated, the cationic copolymers or terpolymers are employed as treating agents. Such pulps as groundwood, unbleached kraft, unbleached sulfite, unbleached Mitchelkirk, semi-bleached kraft, bleached sulfite, alpha-sulfite, rag, unbleached kraft, pulp, bleached hardwood sulfite pulp, or any pulp derived from a mechanical, chemical, or semi-chemical process may be treated with the wet-strength agents of the invention.

The polymers may be added to the pulp either directly as a reaction mass solution or as further diluted solutions, by batch or continuous addition. The required amount of treating agent may be added by gravity flow or by means of pumps, preferably, with some type of metering guide. Flow rates for the diluted treating solutions may be controlled with rotometers or other suitable flow measuring devices such as orifices and weirs. Likewise, the polymer may be supplied to the pulp in controlled amounts by means of reciprocating, proportioning or gear metering pumps.

The wet strength polymers should for best results be added to the paper stock prior to sheet formation, that is, added to the "slush" stock at any point from the beater to the headbox or cylinder vat. In this method of application, uniform distribution of the polymer throughout the pulp is achieved, resulting in uniform wet strength of the paper product. The most satisfactory points of addition of the wet strength polymers of the invention are at the beater, consistency regulator, pulp, bleached hardwood sulfite pulp, or any pulp derived from a mechanical, chemical, or semi-chemical process. It has been determined that the copolymers and terpolymers of the invention are strongly attached to the fibers and held by them when the sheet is formed, and are not separated from the fibers by the vigorous conditions of washing which are imposed by sheet formation.

One excellent property of the polymers of the invention used as wet strength additives is that cure of same upon the paper sheet may be effected even at room temperature. Many prior art materials cannot be cured or permanently affixed to the paper sheet without application of heat. Likewise, the polymers of the invention may also be cured at higher temperatures such as the temperature of formation of a paper sheet from a Fourdrinier papermaking machine. Also, even at the relatively high temperature cures, the polymers of the invention do not coat the paper to an extent whereby the water absorbency of the formed paper product is deleteriously affected.

The polymers of the invention may be added to the paper slurry in amounts as low as 0.001% by weight of active polymer based on the bone-dry weight of the paper. More preferably, the polymers are added at an additional level of at least 0.1% by weight based on the fiber weight. As high as 10.0% by weight of polymer may be added. Generally the effectiveness of the wet strength agents of the invention are proportional to the molecular weight as measured by solution viscosity. Therefore, the highly viscous or higher molecular weight materials need to be added in amounts less than those materials which have a relatively lower molecular weight. Generally, the products of the invention have molecular weights of at least 5,000 and more often have molecular weights ranging above 10,000.

By incorporation with the wet strength agents of the invention the wet and consequently dry strengths of a wide variety of paper products are materially increased. The type of paper product which may be beneficiated by increase in wet strength includes tissue paper, photographic paper, wrappers for moist foods, construction papers, map and blueprint papers, paper fabrics, bags, shower shoes, decorative articles, "disposable" table covers, hand towels, diapers, handkerchiefs, bandages, bed sheets and other paper articles which may take the place of textile fibers, high strength filter paper, cigarette paper, blotting paper, such as desk blotters, tea bag paper, outdoor posters, lens paper, windshiedl wiping tissue, etc.

It has been noted that when high absorbptive capacity is required such as when paper towels and napkins are the paper products treated, these articles have the requisite wet strength, and yet natural absorbptive capacity is not materially altered. Also, in addition to achievement of high tensile strength, it is possible by judicious adjustment of quantities of polymer used, to maintain the paper product in the proper flexible and pliable state. Thus, for example, tissues so treated have the requisite wet and dry strength, and nevertheless are soft and pliable with no hint of abrasive action though tear resistance is materially increased. The wet strength agents of the invention also do not affect the porosity of the paper, and do not impart malodors. In addition, the desired body, and properties of moldability, stiffness, resiliency, and folding number, etc., are not impaired by addition of the wet strength agents. Paper products having incorporated therein the cured wet strength agent, may undergo vigorous manipulation under service and exhibit good stretching ability along with the other above desired properties.

The following examples show typical polymer preparations and their effectiveness as wet strength agents. These examples are meant to be illustrative and the invention, of course, is not limited thereto.

Wet strength performance was measured according to the TAPPI Standards and Suggested Methods: T404M–50 and T456M–49.

Dry and wet tensile strengths were determined on a Towing-Albert Tensile Tester, Model No. 30–LT. The wet strength performances are expressed in terms of percent-ages and are equal to the wet tensile strength x 100 divided by the dry tensile strength.

EXAMPLE I

This example illustrates a typical polymerization carried out so that the copolymer product thereof is soluble in water and particularly soluble in the aqueous reaction media from which it is formed. 45 milliliters of water and 2 millimols of potassium persulfate were placed in a 1 liter, 3 necked flask, arranged with stirrer and thermometer. After purging this flask with nitrogen, 11.1 grams of N-vinyl-2-pyrrolidone and 5.6 grams of distilled acrolein were added, followed by addition of 2 millimols of silver nitrate dissolved in 5 ml. of water. After several minutes of stirring the 2 monomeric reactants together, the temperature rose 5° C. and the liquid reaction mixture became increasingly viscous. 50 ml. of water was then added to the reaction mass. Over a course of 2 hours of reaction time, 350 ml. of additional water were added in incremental additions so that during slightly more than 1/3 of the reaction time the solid concentration of monomers was less than 10%. The temperature during this time was maintained at between 25° C. and 30° C. At the termination of the polymerization 0.1 gram of hydroquinone was added as a stabilizer. The product was a clear, viscous, aqueous liquid containing 3.58% by weight of dissolved copolymer. This particular product when tested for ability to impart wet strength to products
derived from unbleached soft kraft pulp produced a paper product with a 31.4% wet strength. Yet, the excellent wet strength imparted to the paper was achieved by treatment of pulp with polymer as a sole reagent without resort to auxiliary chemicals as alum to aid retention. The water-soluble copolymer was added at a dosage level of 1.0% by weight of active copolymer based on the bone dry weight of the paper fibers.

**EXAMPLE II**

This example is concerned with a preparation of a typical cationic copolymer of the invention. 140 grams of the acrolein-N-pyrrolidone copolymer (3.8% concentration) as prepared in Example I were placed in a 250 ml beaker. 0.15 gram of betaine hydrazide chloride was added to the aqueous copolymer with stirring and with the liquid reaction mixture kept at a temperature of 35–40° C. for a period of 30 minutes. This product was tested on an alpha-sulfite pulp without the use of any aluminum salt. The resultant paper product so treated gave a wet strength of 30.4%. In this case the amine group reacts with the aldehyde group of the copolymer and introduces the quaternary cationic group into the product. In a comparative test a water-soluble bisulfite adduct of polyacrolein, specifically, the sodium bisulfite addition product of acrolein, when tested for effectiveness as a wet strength additive on alpha-sulfite pulp gave a paper product having a wet strength of only 10–12%. This wet strength percent was obtained only when alum was also applied to the paper pulp. When no alum was used in conjunction with the bisulfite adduct of polyacrolein a wet strength of only 3% was obtained. The amount of aluminum sulfate added when employed was 3.0% by weight based on the dry weight of the paper fibers.

**EXAMPLE III**

The particular interpolymer produced in this example was a terpolymer of acrolein, N-vinyl-pyrrolidone and vinyl acetate. Into a 2 liter, 3 necked flask arranged with stirring device and thermometer, were added 95 milliliters of water and 0.54 gram of potassium persulfate. The flask was purged with nitrogen and then 18.7 grams of distilled acrolein, 28.7 grams of distilled vinyl acetate and 25.9 grams of N-vinyl-pyrrolidone were added, followed by addition of 0.34 gram of potassium persulfate dissolved in 5 mL of water. After a period of 25 minutes the temperature slowly rose to a peak of 33° C. and the dilution was then begun slowly. The reaction mixture was diluted over a period of three hours with 1,292 mL of water in such a manner that the solids concentration of reactants was below 10% during the last 1½ hours of reaction time. At the end of the reaction time, the solids content was 3.13% in water. This terpolymer was added at a 1.0% dosage level to unbleached soft kraft pulp and the treated paper product was then measured for wet strength. This product had a wet strength of 30.4%.

**EXAMPLE IV**

This example illustrates preparation of a cationic terpolymer. To 297.0 grams of the terpolymer of Example III (3.13% by weight in aqueous solution) was added 0.09 gram of betaine hydrazide chloride. The cationic material and terpolymer were stirred for 30 minutes at 35–40° C. An alpha-sulfite pulp treated with 1.0% by weight of the above cationic terpolymer when formed into a sheeted paper product had a 31.4% wet strength.

Other water-soluble polymers were also prepared having varying ratios of acrolein, and N-vinyl-pyrrolidone. Likewise, cationic derivatives of the water-soluble copolymers and terpolymers were prepared. Terpolymers of acrolein-N-vinyl pyrrolidone-vinyl-acetate were also prepared in varying mol ratios. Some of these were also modified by reaction with a betaine hydrazide chloride amine-quatemary. All of these copolymers and terpolymers, unmodified or cationically modified, were tested in either alpha-sulfite pulp or unbleached soft kraft pulp without further addition of alum. Wet strength results are presented below in Table I. The above wet strength additives were added at a dosage level of 1.0% by weight based on bone dry weight of paper fibers.

**TABLE I**

<table>
<thead>
<tr>
<th>No.</th>
<th>Monomers</th>
<th>Mol Ratio</th>
<th>Modified By</th>
<th>Wet Strength Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acrolein, NVP</td>
<td>1:3</td>
<td></td>
<td></td>
<td>27.4</td>
</tr>
<tr>
<td>Acrolein, NVP</td>
<td>1:4</td>
<td></td>
<td></td>
<td>22.2</td>
</tr>
<tr>
<td>Acrolein, NVP</td>
<td>1:2</td>
<td></td>
<td></td>
<td>34.4</td>
</tr>
<tr>
<td>Acrolein, NVP</td>
<td>1:1</td>
<td></td>
<td></td>
<td>31.4</td>
</tr>
<tr>
<td>Acrolein, NVP</td>
<td>1:0.6</td>
<td></td>
<td></td>
<td>28.8</td>
</tr>
<tr>
<td>Acrolein, NVP</td>
<td>1:0.6</td>
<td></td>
<td></td>
<td>24.2</td>
</tr>
<tr>
<td>Acrolein, NVP</td>
<td>1:0.6</td>
<td></td>
<td></td>
<td>22.2</td>
</tr>
<tr>
<td>Acrolein, NVP</td>
<td>1:0.6</td>
<td></td>
<td></td>
<td>20.4</td>
</tr>
<tr>
<td>Acrolein, NVP, vinyl acetate</td>
<td>1:1:1</td>
<td></td>
<td></td>
<td>26.4</td>
</tr>
<tr>
<td>Acrolein, NVP, vinyl acetate</td>
<td>1:1:1</td>
<td></td>
<td></td>
<td>28.5</td>
</tr>
<tr>
<td>Acrolein, NVP, vinyl acetate</td>
<td>1:0:7:1</td>
<td></td>
<td></td>
<td>30.4</td>
</tr>
<tr>
<td>Acrolein, NVP, vinyl acetate</td>
<td>1:0:7:1</td>
<td></td>
<td></td>
<td>31.4</td>
</tr>
<tr>
<td>Acrolein, NVP, vinyl acetate</td>
<td>1:0:6:3</td>
<td></td>
<td></td>
<td>26.2</td>
</tr>
</tbody>
</table>

In addition to the specifically shown copolymers and terpolymers, it is possible to prepare compounds of the same class containing other alpha-beta-ethynlyically unsaturated monomers containing a non-ionic hydrophilic side chain radical. Such other compounds may be prepared by the techniques illustrated above. Likewise, these copolymers and terpolymers may be cationically modified with a number of varying amines or amine quarternaries of the type listed above without departing from the scope of the invention.

It has been shown that the novel copolymers and terpolymers described herein are highly effective as wet-strength agents in the absence of alum. It should be further noted, however, that the novel treating agents are equally effective in systems wherein aluminum salts are normally present, such as where alum is used to retain resin size or other materials.

In addition to their primary utility as wet strength agents the copolymers, modified and unmodified, and cationically modified or unreacted terpolymers may be used as additives in a number of processes or employed per se to produce a variety of manufactured articles. For example, the aqueous solutions of polymers may be cast or spun into shaped articles, sheets, films, wrapping tissues, tubing, filaments, yarns, threads, etc. For example, aqueous or alcoholic solutions of the polymers of the invention, by evaporative techniques may be shaped into any desired industrial article. Likewise, the polymers may be used in coating, finishing, casting or molding for adhesion or lamination. Specifically, they may be used as adhesives for cellophane, paper, cloth, etc., as finishes for fabrics, as permanent sizes for yarns, as protective
water resistant coverings, for use as sausage casings, as dye intermediates, as filament film formers, etc. The polymers may also find excellent use as anchoring agents for natural and synthetic filaments, films and artificial leather. The may also be used to finish and impregnate or coat by surface modification or other manipulative techniques, a number of industrial and commercial articles. The versatility of the polymers of the invention in that they may be suitable cured both at room temperature and above, help them find use in many of the above stated processes.

The invention is hereby claimed as follows:

1. As a wet strength agent for paper a composition consisting essentially of a water-soluble product of polymerization of a mixture of monomers having no anionic substituents and consisting of an alpha-beta-ethylenically unsaturated aldehyde having the formula:

$$\text{R}_1 \quad \text{R}_2 \quad \text{CH}=\overset{\cdots}{\text{C}}=\text{CHO}$$

where $\text{R}_1$ and $\text{R}_2$ are selected from the group consisting of halogen, lower alkyl radicals and hydrogen, and a nitrogen heterocycle containing an ethylenically unsaturated group capable of copolymerization with said alpha-beta-ethylenically unsaturated aldehyde.

2. The composition of claim 1 wherein said product is prepared whereby it is soluble in aqueous liquids up to about 10% by weight of solids by carrying out said polymerization as a dilute aqueous reaction mixture containing below about 10% by weight of reactants consisting essentially of said alpha-beta-ethylenically unsaturated aldehyde and said nitrogen heterocycle during at least one-third the period of said polymerization reaction.

3. The composition of claim 1 wherein said alpha-beta-ethylenically unsaturated aldehyde is acrolein and said monomer consisting essentially of 10 to 80 mole percent acrolein and 20 to 90 mole percent of nitrogen heterocycle.

4. As a wet strength agent for paper a cationic composition consisting essentially of a water-soluble reaction product of the copolymer formed by polymerization of a mixture of monomers having no anionic substituent and consisting of an alpha-beta-ethylenically unsaturated aldehyde having the formula:

$$\text{R}_1 \quad \text{R}_2 \quad \text{CH}=\overset{\cdots}{\text{C}}=\text{CHO}$$

wherein $\text{R}_1$ and $\text{R}_2$ are selected from the group consisting of halogen, lower alkyl radicals and hydrogen, and a nitrogen heterocycle containing an ethylenically unsaturated group capable of copolymerization with said alpha-beta-ethylenically unsaturated aldehyde; and a water soluble amine or amine quaternary reactant containing two or more amino groups and of further modification reaction with said copolymer.

5. The composition of claim 4 wherein said cationic composition is prepared whereby it is soluble in aqueous liquids up to about 10% by weight of solids by carrying out said copolymerization as a dilute aqueous reaction mixture containing below about 10% by weight of reactants consisting essentially of said alpha-beta-ethylenically unsaturated aldehyde and said nitrogen heterocycle during at least one-third the period of said polymerization reaction.

6. The composition of claim 4 wherein said alpha-beta-ethylenically unsaturated aldehyde is acrolein, said monomer mixture comprises 20 to 67 mole percent acrolein and 33 to 80 mole percent nitrogen heterocycle, and the ratio of said copolymer said amine reactant ranges from 50:1 to 1:1.

7. As a wet strength agent for paper a terpolymer composition consisting essentially of a water-soluble product of polymerization of a mixture of monomers having no anionic substituents and consisting of an alpha-beta-ethylenically unsaturated aldehyde having the formula:

$$\text{R}_1 \quad \text{R}_2 \quad \text{CH}=\overset{\cdots}{\text{C}}=\text{CHO}$$

wherein $\text{R}_1$ and $\text{R}_2$ are selected from the group consisting of halogen, lower alkyl radicals and hydrogen, a nitrogen heterocycle containing an ethylenically unsaturated group capable of polymerization with said alpha-beta-ethylenically unsaturated aldehyde and an ethylenically unsaturated monomer containing a hydrophilic radical as a side chain, said ethylenically unsaturated monomer capable of a terpolymerization reaction together with said alpha-beta-ethylenically unsaturated aldehyde and said nitrogen heterocycle.

8. The composition of claim 7 wherein said terpolymer is prepared whereby it is soluble in aqueous liquids up to about 10% by weight of solids carrying out said terpolymerization as a dilute aqueous reaction mixture containing below about 10% by weight of reactants consisting essentially of said alpha-beta-ethylenically unsaturated aldehyde, said nitrogen heterocycle and said ethylenically unsaturated monomer during at least one-third the period of said polymerization reaction.

9. The composition of claim 7 wherein said terpolymer is prepared by reacting from about 10% to about 70% mol percent of each of said alpha-beta-ethylenically unsaturated aldehyde, said nitrogen heterocycle and said ethylenically unsaturated monomer.

10. The composition of claim 7 wherein said terpolymer mixture consisting essentially of acrolein, and vinyl pyrrolidone.

11. As a wet strength agent for paper a cationic composition consisting essentially of a water-soluble reaction product of the terpolymer formed by polymerization of a mixture of monomers having no anionic substituents and consisting of an alpha-beta-ethylenically unsaturated aldehyde having the formula:

$$\text{R}_1 \quad \text{R}_2 \quad \text{CH}=\overset{\cdots}{\text{C}}=\text{CHO}$$

wherein $\text{R}_1$ and $\text{R}_2$ are selected from the group consisting of halogen, lower alkyl radicals and hydrogen, a nitrogen heterocycle containing an ethylenically unsaturated group capable of polymerization with said alpha-beta-ethylenically unsaturated aldehyde, and an ethylenically unsaturated monomer containing a hydrophilic radical as a side chain capable of terpolymerization with said alpha-beta-ethylenically unsaturated aldehyde and said nitrogen heterocycle; and a water soluble amine or amine quaternary reactant containing two or more amino groups and capable of further modification reaction with said terpolymer.

12. The method of preparing water-soluble copolymers of an alpha-beta-ethylenically unsaturated aldehyde having the formula:

$$\text{R}_1 \quad \text{R}_2 \quad \text{CH}=\overset{\cdots}{\text{C}}=\text{CHO}$$

where $\text{R}_1$ and $\text{R}_2$ are selected from the group consisting of halogen, hydrogen, and lower alkyl radicals and a nitrogen heterocycle containing an ethylenically unsaturated group capable of copolymerization with said alpha-beta-ethylenically unsaturated aldehyde, said copolymers being useful as wet strength agents for paper, consisting essentially of the steps of preparing an aqueous polymerization reaction mixture of monomers having no anionic substituents and consisting essentially of said alpha-beta-ethylenically unsaturated aldehyde and said nitrogen heterocycle and effecting polymerization of said mixture while keeping the solids concentration below about 10% by weight during at least one-third of the reaction time.

13. The method of claim 12 wherein said reaction is carried out at a temperature range of from 0 to about 60° C. for a period of time ranging from one to three
3,410,828

13

hours duration, said alpha-beta-ethylenically unsaturated aldehyde is acrolein and said nitrogen heterocycle is vinylpyrrolidone, with the monomer mixture comprising 20–67 mole percent acrolein and 33–80 mole percent vinylpyrrolidone.

14. The method of claim 12 wherein said reaction mixture is periodically diluted with water during said polymerization such that during the latter one-half period of said reaction the solids concentration is below about 10% by weight.

15. The method of preparing cationic water-soluble copolymers of an alpha-beta-ethylenically unsaturated aldehyde having the formula:

\[ R_1 \quad \text{R} = \text{CH} = \text{C} - \text{CHO} \]

where \( R_1 \) and \( R_2 \) are selected from the group consisting of halogen, lower alkyl radicals and hydrogen, and a nitrogen heterocycle containing an ethylenically unsaturated group capable of copolymerization with said alpha-beta-ethylenically unsaturated aldehyde, said water-soluble cationic copolymer being useful as wet strengthening agents for paper, consisting essentially of the steps of preparing an aqueous polymerization reaction mixture of monomers having no anionic substituents and consisting essentially of said alpha-beta-ethylenically unsaturated aldehyde and said nitrogen heterocycle, effecting polymerization of said reaction while keeping the solids concentration below about 10% by weight during at least one-third of the reaction time, adding to said produced copolymer an amine capable of further reaction with said copolymer, and reacting said copolymer and said amine whereby said copolymer is rendered substantially cationic.

16. The method of claim 15 wherein said polymerization reaction is carried out at a temperature range from about 0 to 60°C for a period of time ranging from about one hour to about three hours, said alpha-beta-ethylenically unsaturated aldehyde is acrolein, and said nitrogen heterocycle is vinylpyrrolidone, with said mixture comprising 10–80 mole percent acrolein and 20–90 mole percent vinylpyrrolidone.

17. The method of claim 15 wherein said polymerization reaction is carried out while said reaction mixture is diluted with periodic additions of water whereby during the latter one-half of the reaction period the solids concentration is below about 10%.

18. The method of preparing water-soluble terpolymers comprising an alpha-beta-ethylenically unsaturated aldehyde having the following formula:

\[ R_1 \quad \text{R} = \text{CH} = \text{C} - \text{CHO} \]

where \( R_1 \) and \( R_2 \) are selected from a group consisting of halogen, lower alkyl radicals and hydrogen, a nitrogen heterocycle containing an ethylenically unsaturated group capable of copolymerization with said alpha-beta-ethylenically unsaturated aldehyde, and an ethylenically unsaturated monomer containing a hydrophilic radical as a side chain capable of terpolymerization with said alpha-beta-ethylenically unsaturated aldehyde and said nitrogen heterocycle, said terpolymers being useful as wet strengthening agents for paper, consisting essentially of the steps of preparing an aqueous polymerization reaction mixture of monomers having in anionic substituents and consisting essentially of said alpha-beta-ethylenically unsaturated aldehyde, said nitrogen heterocycle and said ethylenically unsaturated monomer, and effecting polymerization of said mixture while keeping the solids content below about 10% by weight during at least one-third of the reaction time.

19. The method of claim 18 wherein said terpolymerization reaction is carried out at a temperature range of from about 0 to about 60°C for a period of time ranging from one to about three hours, said alpha-beta-ethylenically unsaturated aldehyde is acrolein, said nitrogen heterocycle is vinylpyrrolidone, and said ethylenically unsaturated monomer is vinyl acetate, with the mol percents of said reactant monomers being varied from 10 to 70%.

20. The method of claim 18 wherein said terpolymerization reaction is carried out by periodically diluting said reaction mixture with water whereby during the latter half of the reaction time the solids concentration is below about 10%.

21. The method of claim 18 wherein the terpolymer so produced is rendered substantially cationic by adding to said produced terpolymer a water soluble amine or amine quaternary reactant containing two or more amino groups and capable of further reaction with said terpolymer, and reacting said terpolymer and said amine for sufficient time to produce a substantial number of cationic sites in said terpolymer.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,410,828

November 12, 1968

George T. Kekish

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 5, "find acceptance" should read -- find ready acceptance -- line 10, "these effective" should read -- these aldehyde polymers could be so produced whereby they would be effective --; line 38, "aionic" should read -- anionic --. Column 4, line 17, "croton-aldehyde" should read -- crotonaldehyde --; line 25, "en" should read -- an --. Column 6, line 48, "ethyleically" should read -- ethylenically --; line 61, "catioic" should read -- cationic --. Column 9, line 13, "3.8%" should read -- 3.58% --. Column 12, line 44, "reterocycle" should read -- heterocycle --. Column 14, line 8, "ethyelnically" should read -- ethylenically --.

Signed and sealed this 21st day of April 1970.

(SEAL)

Attest:

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