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PREPARATION OF PAPER HAVING IMPROVED WET STRENGTH

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This invention relates to paper, and more particularly to a process for preparing paper having improved wet strength and other improved properties.

Specifically, the invention provides a new and highly efficient process for preparing paper having unexpectedly high wet strength which is of a permanent nature. The process comprises applying to the paper pulp in the beater stage or to the finished paper an aqueous medium containing a water-solubilized polymer of an alpha-beta-ethylenically unsaturated aldehyde, such as an acrolein, which polymer preferably has an intrinsic viscosity of at least 0.5. The invention further provides the improved paper produced by this process.

Ordinary paper when wet loses its strength and is easily torn. In order to overcome this shortcoming, it has become common practice to treat the paper with a nitrogen-containing resin, such as urea- or melamine-formaldehyde resin, that can be subsequently cured to form an insoluble resin. While this method has imparted some improvement in wet strength, it still leaves much to be desired for use on commercial basis. The wet strength provided by this method, for example, is not as high as required for many applications. In addition, the improvement in wet strength is only temporary and is lost after exposure to water. This has been found to be due in part to the fact that the cured nitrogen-containing resin is easily hydrolyzed, particularly in the presence of the acid curing agents remaining in the resin. Further, the paper treated by the above method does not have the desired dimensional stability, fold endurance and tear strength required for certain commercial applications. In some cases, attempts have been made to improve some of these properties by adding more nitrogen-containing resin, but this only tends to make the paper lose its customary feel, appearance and flexibility.

It is, therefore, an object of the invention to provide a new process for producing paper. It is a further object to provide a new process for preparing paper having unexpectedly high wet tensile strengths. It is a further object to provide a new process for preparing paper having a high wet strength that is of a permanent nature and is not lost through hydrolysis. It is a further object to provide a new process for providing wet strength paper that has excellent crease and fold endurance and good dimensional stability. It is a further object to provide a new process for providing wet strength paper that does not require the use of acid curing catalysts. It is a further object to provide a new process for providing wet strength paper that is very efficient and uses only a small amount of resin. It is a further object to provide wet strength paper which has the same feel, appearance and flexibility as the untreated paper. Other objects and advantages of the invention will be apparent from the following detailed description thereof.

It has now been discovered that these and other objects may be accomplished by the process of the invention which comprises applying to the paper pulp or paper, some time during the production of the paper up to and including the finished paper, an aqueous medium containing a water-solubilized polymer of an alpha-beta-ethylenically unsaturated aldehyde, such as acrolein, which polymer preferably has an intrinsic viscosity of at least 0.5, and then allowing the treated paper to dry.

It has been surprisingly found that paper prepared in this manner has unexpectedly high wet tensile strength. Furthermore, the improvement in wet strength is permanent and is not lost through hydrolysis as in the case with the wet strengths obtained by use of the conventional nitrogen-containing resins. Further, the improvement is obtained without change in the feel, absorbency and flexibility of the paper. In addition, the paper treated in the above-described manner has improved dimensional stability, fold endurance and good tear strength. The process is also characterized by its high efficiency, i.e., by the use of only small amount of polymer to obtain the high wet strength values and by the fact that it is operable without the use of any special curing agents.

The solubilized polymers used in the process of the invention are those obtained by treating a substantially water-insoluble polymer of an alpha,beta-ethylenically unsaturated aldehyde described hereinafter with a solubilizing agent to make the polymer water soluble.

The alpha,beta-ethylenically unsaturated aldehydes used in making the basic polymers comprise those aldehydes having an ethylenic group in an alpha-beta-position relative to the aldehyde group, such as, for example, acrolein and alpha and beta-substituted acroleins, such as alpha-ethylacrolein, alpha-isobutylacrolein, alpha-chloroacrolein, beta-phenylacrolein, alpha-decylacrolein, alpha-cyclohexylacrolein and the like. Preferred aldehydes to be employed in making the polymers include the alpha, beta-monoethylenically unsaturated monoaldehydes containing from 3 to 12 carbon atoms, and especially acrolein and the alpha and beta-substituted acroleins wherein the substituent on the alpha and/or beta positions is an alkyl, cycloalkyl or aryl group containing no more than 8 carbon atoms. 2-alkenals containing up to 8 carbon atoms come under special consideration.

The polymers of the above-described aldehydes may be obtained by a variety of methods. They may be obtained, for example, by treating the unsaturated aldehyde with free radical yielding catalysts, by the use of redox polymerization systems, by the addition of ionic type polymerization initiators and the like. The polymerization may also be effected in bulk, solvent or aqueous emulsion or suspensions systems.

A preferred method for polymerizing the unsaturated aldehydes comprises contacting the aldehyde with a free radical yielding catalyst at a temperature below about 30° C. and in the presence of a material possessing an OH group.

The catalyst employed in the polymerization may be any free radical yielding catalysts. Examples of such catalysts include, among others, the peroxides, such as benzoyl peroxide, hydrogen peroxide, potassium persulfate, alkali perborates, diacetyl peroxide, tertiary butyl hydroperoxide, tertiary amyl hydroperoxide, ditertiary butyl peroxide, ditertiary hexyl peroxide, acetyl benzoyl peroxide, cumene hydroperoxide, tetralin hydroperoxide, phenylcyclohexane hydroperoxide, tertiary-butylisopropylbenzene hydroperoxide, tertiary butyl peracetate, tertiary butyl perbenzoate, ditertiary butyl phthalate, ditertiary butyl peradipate, tertiary butyl percarbonate and the like, and azo catalysts, such as organic compounds containing a —N=N— group as alpha,alpha'-azodiisobutyronitrile, alpha,alpha' - diisobutyrate, alpha, alpha' - azobis(alpha,gamma - dimethylvaleronitrile, alpha,alpha' - azodiisobutyroamide, alpha,alpha - azobis(alpha - cyclopropylpropionitrile), alpha,alpha' - (alpha-methyl - beta - phenylpropionitrile), alpha(carbamylazo)isobutyronitrile, alpha,alpha - azobis(alpha - cyclohexylpropionitrile), 1,1' - azodicyclohexanecarbonitrile, diazoaminobenzene, 1,1'-azobis(1-phenylethane) and the like, various aldoximes and ketoximes, azines and the like.

Particularly preferred catalysts to be employed include the organic peroxides as those of the formula

R—O—O—R′

wherein R is an alkyl, cycloalkyl or aryl group and R′ is hydrogen, alkaryl, cycloalkyl, aryl or alkaryl groups, preferably containing no more than 10 carbon atoms each, and alkyl peresters of percarboxylic acids as well as the aliphatic and aromatic type bisaco compounds as the bisaconitriles and particularly those wherein the nitrogen of the group —N=N— is attached to aliphatic and cycloaliphatic carbon atoms.

The above-described catalysts are employed in small amounts, the exact amount being dependent upon the particular type selected. In general, the amount of the catalyst used will vary from about 0.1% to about 5% by weight of the material being polymerized. Preferred amounts vary from 0.5% to 3% by weight of the material being polymerized.

The polymerization of the unsaturated aldehyde is conducted in the presence of material possessing an OH group. This material may be water and alcohols, carboxylic acids or the like, such as, for example, cyclohexanol, ethanol, acetic acid, propionic acid, ethylene glycol, benzoic acid, 1,5-pentanediol, hexylene glycol, allyl alcohol and its polymers, glycerol, 1,4-butanediol and the like. The amount of the hydroxy-containing material can be as low as 2% by weight of the material being polymerized as long as the conversion of the polymer is kept low, e.g., below about 10% conversion. The amount of the hydroxy-containing material may go as high or higher than 75% by weight of the material being polymerized, the exact amount employed being determined by the type of polymer structure desired as noted hereinafter. When larger amounts of the hydroxy-containing material are employed, e.g., at least 10% by weight, the conversion of monomer to polymer can be relatively high and may even be taken up to 100%.

It is also desirable in some cases to include in the reaction medium minor amounts of other monoethylenically unsaturated monomers which will undergo copolymerization with the unsaturated aldehydes. Examples of these include, among others, vinylpyridine, styrene, allyl alcohol, acrylic and methacrylic acids and their alkyl esters, vinyl acetate, monoolefins, allyl esters of monocarboxylic acids, vinyl halides, acrylonitrile, methacrylonitrile and the like and mixtures thereof. These monomers are preferably employed in amounts varying from about 0.1% to 25% by weight of the monomers being polymerized. Minor amounts of polyethylenically unsaturated compounds, such as butadiene, isoprene and the like may also be employed.

The polymerization is effected by bringing the unsaturated aldehyde (and other monomer or monomers if desired), free radical yielding catalyst and material having the OH group, together preferably with stirring and then maintaining the temperature of the mixture below 30° C. Preferred temperatures range from about 0° C. to 25° C. and still more preferably temperatures ranging from about 10° C. to 25° C. Temperatures are maintained within this range preferably by means of cooling as by condensors, water batch and the like. Atmospheric, superatmospheric and subatmospheric pressures may be utilized as desired.

The polymerization is preferably accomplished in an inert atmosphere. This is preferably accomplished by passing inert gases, such as nitrogen, through the reaction vessel during the polymerization.

The high molecular weight polymers will generally precipitate out as a white solid and may be recovered by any suitable means, such as filtration, centrifugation and the like. After recovery, the polymer may be washed with water, ketones, ethers and the like to remove any impurities.

The preparation of some of the polymers of unsaturated aldehydes by this method is illustrated below.

POLYMER A

1 mole of freshly distilled acrolein was combined with 1 mole of acetic acid and 1.5 parts of azobis(isobutyronitrile) and the mixture kept at room temperature in the dark for several hours. A white solid precipitated during this time. The polymer was recovered by filtering and washing with water and acetone. The resulting product was a fine white powder. Analysis of the solubilized form indicated the polymer had an intrinsic viscosity of .6.

POLYMER B

71 parts of freshly distilled acrolein was combined with 60 parts of acetic acid and 1.5 parts of azobis(isobutyronitrile) and the mixture kept at room temperature in the dark and in the presence of nitrogen for several hours. The mixture is then filtered and the white solid that was recovered was washed with water and acetone. Analysis of the solubilized form indicated that this polymer had an intrinsic viscosity of 1.1.

POLYMER C

1500 parts of freshly distilled acrolein was combined with 1500 parts of acetic acid and 10 parts of azobis(isobutyronitrile) and the mixture kept at room temperature in the dark and in the presence of nitrogen for several hours. The mixture is then filtered and the product washed with water and acetone. Analysis of the solubilized form indicated that this polymer had an intrinsic viscosity of 1.47.

POLYMER D

100 parts of freshly distilled acrolein was combined with 10 parts of benzyl alcohol and 1 part of azobis(isobutyronitrile) and the mixture stirred and maintained at about 30° C. The white powdered polymer precipitated. The product was washed and dried. Analysis indicated that the polymer had an intrinsic viscosity of about 0.60.

POLYMER E

100 parts of freshly distilled acrolein was combined with 0.5 part of benzoyl peroxide and 10 parts of methanol and the mixture maintained at room temperature for about 3 hours. The white solid that precipitated was washed and dried. Analysis of the solubilized form indicated that this polymer had an intrinsic viscosity of 0.60.

Another method for preparing polymers of the unsaturated aldehydes which is particularly preferred comprises treating the unsaturated aldehyde in an aqueous system with a redox polymerization catalyst, a chelating agent and preferably an emulsifying agent. The process preferably employs a free-radical polymerization catalyst, a multivalent metal in the lowest valent state, and a chelating agent. Anti-coalescent agents, such as nonionic, cationic or anionic agents may also be employed.

Examples of free radical yielding catalysts that may be employed include, among others, peroxides, such as benzoyl peroxide, hydrogen peroxide, potassium persulfate, potassium permanganate, methyl cyclohexyl peroxide, alkali perborates, diacetyl peroxide, tertiary butyl hydroperoxide, tertiary amyl hydroperoxide, ditertiary butyl peroxide, ditertiary hexyl peroxide, acetyl benzoyl peroxide, cumene hydroperoxide, tetralin hydroperoxide, phenylcyclohexane hydroperoxide, tertiary-butylisopropylbenzene hydroperoxide, tertiary butyl peracetate, tertiary butyl perbenzoate, ditertiary butyl phthalate, ditertiary butyl peradipate, tertiary butyl percarbonate and the like. Particularly preferred free radical yielding catalysts include the organic peroxides, such as the dialkyl peroxides, diaryl peroxides, tertiary alkyl hydroperoxides, alkyl peresters of percarboxylic acids, and particularly those of the above-noted group which contain no more than 18 carbon atoms per molecule.

The above-described catalysts are employed in small

amounts, the exact amount being dependent upon the particular type selected. In general, the amount of catalyst used will vary from about 1×10^{-6} to about 2×10^{-2} mols per mol of unsaturated aldehyde being polymerized. Preferred amounts vary from about 1×10^{-3} to 1×10^{-4} mols per mol of material being polymerized.

A salt of a multivalent metal is also a component of the catalyst system. By multivalent metal is meant one that can change its valence state reversibly. Examples of such metals include iron, manganese, copper, vanadium cobalt, nickel, tin, silver, titanium, etc. When added to the reaction mixture, the metal must be at least in part in a lower valence state such as, for example, ferrous chloride, silver nitrate, titanium dichloride, cobaltous chloride, ferrous pyrophosphate, potassium ferrocyanide, manganous sulfate, ferrous sulfate, and the like. The anion portion of the metal salt may be of any type as long as the resulting salt has the necessary solubility in the reaction medium.

The amount of the metal salt employed will depend upon the amount of the peroxide catalyst utilized. It is preferred to have one gram ion of the metal per mol of the peroxide catalysts, and more preferably from .5 to 1 gram ion per mol of peroxide.

Another essential component of the reaction mixture is a chelating agent, i.e., a material which forms a complex with polyvalent metal ions; that is the material and the metal ion unite through coordinate linkages stable in aqueous systems. These compounds are described in detail in Martell and Colvin, "Chemistry of the Metal Chelate Compounds" (1952). These materials possess at least one and preferably a plurality of electron-donating groups. The elements in such groups preferably fall in Groups V and VI of the periodic table, such as, for example, nitrogen, oxygen and sulfur. Examples of such chelating agents include, among others, metal cyanides, such as potassium, sodium, lithium and alkali metal and alkaline earth metal cyanides, and corresponding cyanates and thiocyanates, as well as malonic acid, ethylmalonic acid, diethylmalonic acid, 8-hydroxyquinoline, dimethylglyoxime, ethylene diamine, trimethylenediamine and their substituted products, such as diacetonediamine, diethylenetriamine, N,N-diethylethylene diamine, triethylene tetramine, propylenediamine, tris(2-aminoethyl)amine, 1,2,3-triaminopropane, N(3-amino-2-hydroxypropyl)-2-hydroxy-1,3-propanediamine, N,N'-di(hydroxypropyl) diethylene triamine, bipyridyl, o-phenanthroline, amino acids as glycine, alanine, beta-alanine, asparagine, blutamic acid, glycylglycine, phenylalanine, ammonia diacetic acid, ammonia triacetic acid, ethylenediamine tetracetic acid, ammonia dipropionic acid, ethylene diamine dipropionic acid, 1,3-diaminocyclohexane-N,N'-tetracetic acid, 3-sulfonaniline diacetic acid, aniline diacetic acid, 4-aminobenzoic acid-N,N-diacetic acid, beta-aminoethylphosphonic acid-N,N-diacetic acid, glycine-N-propionic acid, N-benzylethylenediamine triacetic acid and methylamine-N,N-diacetic acid, salicylaldehyde, 3-n-propylsalicylaldehyde, 3-ethoxysalicylaldehyde, 2-hydroxy-1-naphthaldehyde, acetylacetone, trifluoroacetylacetone, benzoylacetone, ethylacetoacetate, acetic acid, propionic acid, oxalic acid, phthalic acid, succinic acid, citraconic acid, 5-chloro-1,10-phenanthroline, 5-phenyl-1,10-phenanthroline, glycylglycidylglycine, histidine, methionine, proline, serine, tryptophan, tyrosine, glyconic acid, beta-hydroxybutyric acid, salicylic acid, 5-sulfosalicylic acid, aminophenol, and 3,6-disulfo-1,8-dihydroxynaphthalene.

Preferred chelating agents to be employed are these which are effective in neutral and acid media and which form with polyvalent metals one or more pentatomic or hexatomic heterocyclic rings containing the metal as one of the components of the ring or rings. These preferred materials also possess a plurality of electron-donating groups, such as, for example, those containing N, O or S, such as amino groups, OH groups, aldehyde groups, and the like.

Preferred chelating agents to be employed are these which are effective in neutral and acid media and which form with polyvalent metals one or more pentatomic or hexatomic heterocyclic rings containing the metal as one of the components of the ring or rings. These preferred materials also possess a plurality of electron-donating groups, such as, for example, those containing N, O or S, such as amino groups, OH groups, aldehyde groups, and the like.

Especially preferred are chelating agents containing nitrogen and carboxyl groups which carboxyl groups appear in the form of partially or wholly neutralized form as with sodium, potassium or alkali metal salts (including ammonium). Examples of these include, among others, the sodium and potassium salts of ammonia diacetic acid, ammonia triacetic acid, ethylene diamine tetraacetic acid, ammonia dipropionic acid, ethylene diamine dipropionic acid, 1,3-diaminocyclohexane-N,N-tetraacetic acid, 3-sulfoaniline diacetic acid, aniline diacetic acid, 4-aminobenzoic acid-N,N-diacetic acid, betaaminoethylphosphonic acid-N,N-diacetic acid, glycine-N-propionic acid and the like, and mixtures thereof.

The amount of the chelating agent employed will depend on the amount of the metal salt employed. It is preferred to have at least one mol of the chelating agent per gram ion of the metal present. More preferably, from 1 to 1.5 mols of the chelating agent is employed per gram ion of metal present.

Particularly superior results are obtained when an anticoalescent agent is included in the reaction mixture. The presence of such materials effects unexpectedly an enhanced rate of polymerization and maintenance of molecular weight. The agent may be a cationic, anionic or non-ionic material and have a great variety of different compositions. Preferred materials include the ionic agents and especially those having a polar structure including a hydrophilic (predominantly hydrocarbon) residue and a charged (ionic) radical thereon, such as anionic surface active compounds including alkali metal and nitrogen-base soaps of higher fatty acids, such as potassium, and sodium myristate, laurate, palmitate, oleate, stearate, ammonium stearate, etc., as well as the surface-active compounds of the cation-active variety, such as salts of long-chain aliphatic amines and quaternary ammonium bases, such as lauryl amine hydrochloride, stearyl amine hydrochloride, palmityl amine hydrobromide. Additional examples of suitable ionic surface-active agents include the alkali metal or ammonium alkyl or alkylene sulfates or sulfonates, such as sodium and/or potassium lauryl sulfate, alkyl, aryl and alkylated arylsulfonates, cetyl sulfonate, oleylsulfonate, stearylsulfonate, sulfonated Turkey red oil, sulfonated mineral oils, sodium, potassium and ammonium isopropyl naphthalene sulfonate, amine-substituted alcohol, sulfonated fatty esters and amides, the hydrochloride of diethyl aminoethyloleylamide, trimethylcetyl ammonium methyl sulfate, alkanesulfonic acids, alkali metal and ammonium salts of sulphonated long-chain hydrocarbons, or sulphonated long-chain fatty acids, such as sulphonated oleic acid and the sodium, potassium and ammonium salts of sulphated cetyl alcohol.

Also preferred are the non-ionic surface active agents, i.e., those which are not salts and are not subject to ionization when added to water. Examples of these agents include, among others, partial esters of polyhydric alcohols and saturated or unsaturated fatty acids and preferably fatty acids containing at least and more preferably from 12 to 18 carbon atoms, and hexitans and hexitides such as sorbitan or mannitan monolaurate, monopalmitate, monostearate, monooleate or the monoesters of coconut oil fatty acids and the like products described in U.S. 2,322,820. Other examples of partial esters of this type include the pentaerythritol mono- and dipalmitate, pentaerythritol mono- and distearate, pentaerythritol mono- and dioleate, 1,2,6-hexanetriol mono- and dicaproate, 1,2,6-hexanetriol mono- and di-

oleate, trimethylolpropane distearate, trimethylolpropane dilaurylate, polyglycerol dilaurate, inositol monolaurate, glucose monostearate, sucrose monooleate, polyglycol monooleate, polyglycol monostearate, and the like.

Examples of other suitable non-ionic agents include the hydroxypolyoxyalkylene ethers of the above-described partial esters. Specific examples of this include, among others, the polyethylene glycol ethers of sorbitan or mannitan monolaurate, monopalmitate, monooleate or monostearate. Other examples include the polyethylene glycol ethers or pentaerythritol mono-and dipalmitate, pentaerythritol mono- and distearate, trimethylolpropane distearate, polyglycerol dilaurate, inositol monolaurate and the like.

Other examples include the hydroxypolyoxyalkylene ethers of phenols, such as the reaction product of ethylene oxide and/or propylene oxide and phenols as phenol, bis-phenol-A, resorcinol, and the like, and mixtures thereof.

Other examples include di- and monoethers of polyhydric compounds and particularly the polyalkylene glycols. Especially preferred are the aryl and alkaryl polyethylene glycol ethers, such as phenyl polyethylene glycol monoether, xylylpolyethylene glycol monoether, alkyl phenyl polyalkylene glycol ethers, such as nonyl phenyl polyethylene glycol ether, isopropylphenyl polyethylene glycol monoether and the like.

Especially preferred materials to be used, particularly because of the superior results obtained therewith such as surprisingly rapid rate of polymerization include the water-soluble agents as polyethylene oxides, polyacrylamides, starch, casein, styrene-maleic anhydride copolymers and methocell.

The amount of the anti-coalescent agent employed in the polymerization process will vary over a considerable range depending upon the unsaturated aldehyde to be polymerized and the particular agent selected. In general, the amount of the emulsifying agent will vary from about .1% to 80% by weight of the unsaturated aldehyde. Preferred amounts vary from .5% to 25% by weight of the monomer.

It is also desirable in some cases to include in the reaction medium minor amounts of other monoethylenically unsaturated monomers which will undergo copolymerization with the unsaturated aldehydes. Examples of these include, among others, vinylpyridine, styrene, allyl alcohol, acrylic and methacrylic acids and their alkyl esters, vinyl acetate, monoolefins, allyl esters of monocarboxylic acids, vinyl halides, acrylonitrile, methacrylonitrile and the like and mixtures thereof. These monomers are preferably employed in amounts varying from about 0.1% to 25% by weight of the monomers being polymerized. Minor amounts of polyethylenically unsaturated compounds, such as butadiene, isoprene and the like may also be employed.

The polymerization may be conducted in non-basic liquid media, but is preferably conducted in an aqueous system. The amount of water employed may vary considerably. Preferably one employs from 100 to 500 parts of water per 100 parts of monomer to be polymerized.

The temperature employed in the process may also vary over a considerable range. It is generally preferred to employ relatively low temperatures. In general, temperatures will vary from the freezing point of the reaction mixture to about from 50° C. Preferred temperatures range from about 0° C. to 45° C. Atmospheric, superatmospheric and subatmospheric pressures may be utilized as desired.

The polymerization is preferably effected in an inert atmosphere. This may preferably be accomplished by passing inert gases such as nitrogen, methane, etc. into and through the reaction mixture.

The polymer will precipitate out as a white solid and may be recovered by any suitable means, such as filtration, centrifugation and the like. After recovery, it is generally desirable to wash the polymer with water and acetone and then dry the product.

Preparation of some of the polymers by this redox system is illustrated below:

POLYMER F

1000 parts of freshly distilled acrolein was combined with 1500 parts of water and 2.73 parts of potassium persulfate and 2.02 parts of $FeCl_2$-hydrate, 10 parts of a nonyl phenol-alkylene oxide condensate and 4 parts of disodium salt of ethylene diamine tetraacetic acid. This mixture was maintained at room temperature for several hours. The mixture is then filtered and washed with water and dried. Analysis of the solubilized form of the polymer indicated the polymer had an intrinsic viscosity of about 1.48.

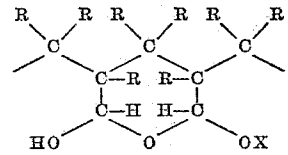
POLYMER G

100 parts of freshly distilled acrolein was added to 300 parts of water and to this mixture was added .272 part potassium persulfate, .203 part of ferrous chloride tetrahydrate and .4 part of disodium salt of ethylene diamine tetraacetic acid. The resulting mixture was stirred for 24 hours at 0° C. under an atmosphere of nitrogen. During that period a white solid precipitated. The mixture was filtered and the product washed and dried. Analysis of the solubilized form of the polymer indicated the polymer had an intrinsic viscosity of about 2.4.

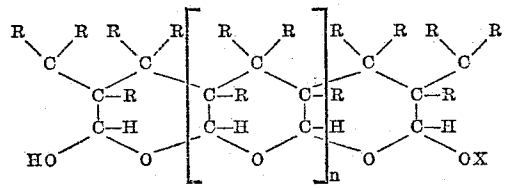
POLYMER H

100 parts of acrolein was added to 325 parts of water and to this mixture was added 2.27 parts of potassium persulfate, 2.002 parts of ferrous chloride tetrahydrate and 4 parts of disodium salt of ethylene diamine tetraacetic acid. This mixture was kept at room temperature for 6 hours with stirring and under an atmosphere of nitrogen. The white solid that precipitated was removed, washed and dried. Analysis of the solubilized form indicated the product had an intrinsic viscosity of 1.02.

The polymers of the unsaturated aldehydes used in making the water-soluble derivatives useful in the process of the invention are preferably the solid polymers of the alpha, beta-unsaturated aldehydes which possess over 95% and preferably 97–99.5% or greater percent theoretical aldehyde function, i.e., when the polymer is subjected to conventional test for presence of aldehyde groups (e.g., addition of hydroxylamine hydrochloride and titrate liberated water with Karl Fischer reagent) the results show that over 95% of the theoretical aldehyde groups present by addition polymerization at the double bond are present in the polymer as such or in hydrated form. Further analysis has shown that the polymer contains many groups wherein the aldehyde is in a hydrated form as



and



wherein n is integer from 0 to 5, X is hydrogen, an acyl

group or hydroxy containing radical (depending on OH containing material used in preparation of the polymer) and R is hydrogen or hydrocarbon and particularly alkyl, cycloalkyl and aryl radicals containing from 1 to 10 carbon atoms.

The above polymers also have relatively high molecular weights. The preferred ones are those having an intrinsic viscosity of at least 0.5, and preferably 0.8 to 3.0. Particularly superior results are obtained with polymers having an IV between 1.1 and 1.8. These values are determined by the conventional technique of polyelectrolyte viscosity measurements at 25° C. Polymers of lower molecular weight, such as those having intrinsic viscosity between 0.1 to 0.5 can be employed, particularly if additional steps are taken to modify the product as shown below.

The water-soluble derivatives of the above-described water-insoluble polymers may be obtained by a variety of methods. They are preferably prepared by suspending the polymer in an aqueous solution containing the water-solubilizing agents, such as, for example, sulfur dioxide or an alkali bisulfite, such as sodium bisulfite, The amount of the polymer added will vary depending on the particular agent involved and the concentration of the agent. In general, it is preferred to add from 1 to 50 parts of the polymer per 100 parts of water. The concentration of the solubilizing agent will generally vary from about 1% to 25%. Stirring and heating may be applied to assist in the dissolution. Temperatures employed will generally vary from about 20° C. to about 90° C. Various other means, such as addition of small amounts of acid catalysts or the addition of swelling agents such as acetone, tetrahydrofuran, and the like, may also be employed to assist in the dissolution.

The preparation of several solubilized derivatives is illustrated below.

SOLUBILIZED POLYMER A

10 parts of Polymer A was suspended in water so as to form a 10% slurry. SO_2 was bubbled into the solution at room temperature for about one hour. The container was sealed and stirred for 24 hours. By that time the polymer had gone into solution. This polymer had an intrinsic viscosity of 0.60.

SOLUBILIZED POLYMER B

10 parts of Polymer B was suspended in water to form a 10% aqueous slurry. Sulfur dioxide was bubbled into the solution at room temperature for about one hour. The container was sealed and stirred for 24 hours. At that time, the polymer had gone into solution. This polymer had an intrinsic viscosity of 1.1.

SOLUBILIZED POLYMER C

10 parts of Polymer C was suspended in water to form a 10% aqueous slurry. 5 parts of sodium bisulfite were added and the mixture kept at room temperature. The mixture was stirred for several hours until the polymer had gone into solution. This polymer had an intrinsic viscosity of 1.47.

SOLUBILIZED POLYMER D

10 parts of Polymer A was suspended in water to form a 10% aqueous slurry. Sulfur dioxide was bubbled into the solution at room temperature for about one hour. The container was sealed and stirred for 24 hours. By that time, the polymer had gone into solution. This polymer had an intrinsic viscosity of 0.60.

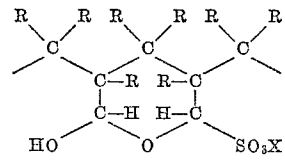
SOLUBILIZED POLYMER E

10 parts of Polymer E was suspended in water to form a 10% aqueous slurry. Sulfur dioxide was bubbled into the solution at room temperature for about one hour. The container was sealed and stirred for 24 hours. By that time, the polymer had gone into solution. This polymer had an intrinsic viscosity of 0.60.

SOLUBILIZED POLYMER F

10 parts of Polymer F was suspended in water to form a 10% aqueous slurry. Sulfur dioxide was bubbled into the solution at room temperature for about one hour. The container was sealed and stirred for 24 hours. By that time, the polymer had gone into solution. This polymer had an intrinsic viscosity of 1.48.

The water-soluble derivatives of the polymers will have substantially the same molecular weight of the basic water-insoluble polymer. In the case of the sulfur dioxide and bisulfite used in the dissolution, the polymer will also contain a plurality of free sulfonic acid groups or water-soluble salt sulfonate groups contained in the polymer molecule and the product may therefore be regarded as a polymeric polysulfonic acid and polymeric polysulfonate metal salt. For example, the polymer will contain



groups, wherein the R is as described above and X is hydrogen or alkali metal.

In some cases, it may be desirable to further modify the water-soluble derivatives to improve their effectiveness for the treatment of paper. This may be particularly true if the basic polymer is one that has a low molecular weight. This is also true in cases where it is desired to use the polymer in the beater stage and it is desirable to improve the substantivity of the polymer to the paper pulp.

The modification can be accomplished in several ways, such as, for example, by addition of hydrogen sulfide, alcohols, amines, metal salts and the like. This type of modification is illustrated by the following:

H_2S-MODIFIED WATER-SOLUBLE POLYMER

200 parts (11.2 parts solids) of water solution of a polyacrolein solubilized with sulfur dioxide and having an intrinsic viscosity of 0.54 was stirred while gaseous hydrogen sulfide was bubbled into the solution. A precipitate formed. After 2 hours the hydrogen sulfide addition was stopped and a stream of nitrogen was passed for ten minutes to remove excess hydrogen sulfide. The mixture was centrifuged to remove the precipitate and the resulting solution containing the modified polymer was employed for the treatment of paper.

ALCOHOL-MODIFIED WATER-SOLUBLE POLYMER

200 parts (11.2 parts solids) of a water solution of a polyacrolein solubilized with sulfur dioxide and having an intrinsic viscosity of 0.54 was combined with 100 parts of isopropyl alcohol and the mixture refluxed for 30 minutes. The excess water and isopropyl alcohol was removed leaving a light yellow solid which had a sulfur content of 3.72% compared to 5.39% for the original polymer.

The aqueous solutions of the above-described solubilized polymers which are used for the treatment of paper may be prepared by any suitable method. They are preferably prepared by adding water to the solubilized polymer solution to form water solutions having the desired concentration. The concentrations of the solutions preferably vary from 0.1% to 5% aqueous solutions. Particularly superior results are obtained by the use of concentrations varying from about 0.5% to 2.5% by weight.

The water solution used in the treatment of the paper may be basic, neutral or acidic. It is generally preferred

to employ acidic solutions, e.g., those having a pH between 1.8 and 5. Particularly superior results are obtained, both in the dipping process and in the beater stage addition process, by first neutralizing the solution containing the water-soluble polymer derivative and then adding a polyvalent metal salt, such as, for example, aluminum sulfate, zinc nitrate and the like. When this technique is used, much higher wet strength retention values are obtained as compared to those obtained by using the usual procedure with the unmodified polymeric solutions.

Emulsifying agents, water-dispersible binding colloids, plasticizers, anti-oxidants, dyes, fillers, etc. may also be included in the aqueous system, but are not essential to obtaining the results set out above.

As indicated above, the aqueous system containing the solubilized polymer may be applied to the paper pulp or paper at any stage during the preparation of the paper up to and including the finished paper.

If the polymer is to be added to the beater stage preferable to taking steps to increase substantivity of the polymer to cellulosic materials such as by modification of the polymer as by adding amines, hydrogen sulfide, alcohols and the like as noted hereinabove, or by modifying conditions or the pulp as by adding polyvalent metal salts as alum, etc. Preferably the aqueous medium is added during the beater stage when the suspension of the paper pulp is being rapidly agitated or are added directly to the finished sized or unsized paper. If the materials are added during the beater stage the beater operations may be any of those now used for this purpose. One merely needs to pour or otherwise add the solubilized polymer, preferably in the form of an aqueous medium, directly to the aqueous suspension of pulp either all at once or intermittently over a short period of time.

If the aqueous system is to be applied to the finished paper, it may be added by spraying, by rollers, by dipping or by running the paper through a conventional-type padding apparatus. Amount of pick-up will vary, but in most cases vary from about 50% to 100% based on the weight of paper.

After the aqueous system has been applied to the paper as indicated above, the treated product is then subsequently dried to effect the cure. The drying may be accomplished by merely rolling or squeezing off the excess solution and then setting out the paper in the air to dry, or by use of forced air. Temperatures used in the drying may vary from about room temperature, e.g., about 20° C. to 100° C. The period of drying will depend largely on the amount of pick-up and concentration of the polymer solution. In most instances, drying periods of from about 1 to 30 minutes should be sufficient.

Any type of paper may be treated according to the process of the invention. Examples of such paper include, for example, those prepared from wood, cotton, linen, hemp, jute, mulberry, straw, bamboo and cane fibers or mixtures thereof, by any of the known processes such as the sulfate process, soda process, sulfite process. The paper may be colored or white and may be further treated for special applications.

The paper treated according to the process of the invention may be used for a variety of applications such as facial tissue, hand towels, maps, filing cards, construction paper, wrapping paper, containers and the like. Because of its resistance to hydrolysis and relative non-toxic nature, the paper is particularly suited for use in preparing wrapper or containers for food.

To illustrate the manner in which the invention may be carried out, the following examples are given. It is to be understood, however, that the examples are for the purpose of illustration and the invention is not to be regarded as limited to any of the specific materials or conditions recited therein.

Example I

This example illustrates the improvement in properties obtained by treating bleached sulfite paper with solubilized Polymer A.

A 1%, 2% and 3% water solution of solubilized Polymer A was prepared by adding additional water to the SO_2-solubilized polymer solution prepared as shown above. Sheets of bleached sulfite paper were then passed into and through the water solution so as to effect a 100% wet pick-up. The sheets were pressed out on dry paper and then allowed to dry at room temperature.

The resulting sheets had the appearance, feet and flexibility of the untreated paper, but demonstrated suprising improvement in fold endurance, dimensional stability, resistance to hydrolysis and improvement in wet strength. The improvement in wet strength is shown in the following table:

Solution, Percent	Dry Strength	Wet Strength	Percent Strength Retention
1	16.0	8.0	50
2	18.3	9.3	51
3	18.9	10.4	61

A similar sheet of bleached sulfite paper was treated with an aqueous solution of amine modified urea-formaldehyde resin and aluminum sulfate as catalyst. The improvement in wet strength in this case was as follows:

Solution, Percent	Dry Strength	Wet Strength	Percent Strength Retention
1	11.2	3.0	27
2	12.6	4.0	35
3	14.4	5.2	36

A comparison of the results in the above tables indicates the superior improvement obtained by the claimed products over the conventional paper treating agents.

Example II

This example illustrates the improvement in properties obtained by treating bleached sulfite paper with solubilized Polymer B.

A 1% and 2% water solution of solubilized Polymer B was prepared by adding additional water to the SO_2-solubilized Polymer B prepared as shown above. Sheets of bleached sulfite paper were then passed into and through the water solution so as to effect a 100% pick-up. The sheets were pressed out on dry paper and allowed to dry at room temperature.

The resulting sheets had the appearance, feel and flexibility of the untreated paper, but demonstrated suprising improvement in wet strength, fold endurance, dimensional stability and resistance to loss of wet strength properties on prolonged exposure to water. The improvement in wet strength is shown in the following table:

Solution, Percent	Dry Strength	Wet Strength	Percent Strength Retention
1	12.6	6.4	51
2	10.8	5.8	54
Control	10.2	0.4	

Example III

This example illustrates the improvement in properties obtained by treating bleached sulfite paper with solubilized Polymer C.

A .75% and 2% water solution of solubilized Polymer C was prepared by adding additional water to the solubilized Polymer C prepared as shown above. Sheets of bleached sulfite paper were then passed into and through the water solution so as to effect a 100% wet pick-up. The sheets were pressed out on dry paper and then allowed to dry at room temperature.

The resulting sheets had the appearance, feel and flexibility of the untreated paper, but demonstrated suprising improvement in fold endurance, dimensional stability, resistance to hydrolysis and improvement in wet strength. The improvement in wet strength is shown in the following table:

Solution, Percent	Dry Strength	Wet Strength	Percent Strength Retention
.75	15.4	7.0	45
3	13.2	10.2	77
Control	10.2	0.4	

Example IV

This example illustrates the improvement in properties obtained by treating bleached sulfite paper with solubilized Polymer D.

A 1% and 2% water solution of solubilized Polymer D was prepared by adding additional water to the solubilized Polymer D prepared as shown above. Sheets of bleached sulfite paper were then passed into and through the water solution so as to effect a 100% pick-up. The sheets were pressed out on dry paper and allowed to dry at room temperature.

The resulting sheets had the appearance, feel and flexibility of the untreated paper, but demonstrated surprising improvement in wet strength, fold endurance, dimensional stability and resistance to loss of wet strength properties on prolonged exposure to water. The improvement in wet strength is shown in the following table:

Solution, Percent	Dry Strength	Wet Strength	Percent Strength Retention
1	12.8	6.4	50
2	13.2	6.6	50
Control	10.2	0.4	

Example V

This example illustrates the improvement in properties obtained by treating bleached sulfite paper with solubilized Polymer E.

A 1% and 2% water solution of solubilized Polymer E was prepared by adding additional water to the solubilized Polymer E prepared as shown above. Sheets of bleached sulfite paper were then passed into and through the water solution so as to effect a 100% pick-up. The sheets were pressed out on dry paper and allowed to dry at room temperature.

The resulting sheets had the appearance, feel and flexibility of the untreated paper, but demonstrated surprising improvement in wet strength, fold endurance, dimensional stability and resistance to loss of wet strength properties on prolonged exposure to water. The improvement in wet strength is shown in the following table:

Solution, Percent	Dry Strength	Wet Strength	Percent Strength Retention
1	12.4	4.4	35

Example VI

This example illustrates the improvement in properties obtained by treating bleached sulfite paper with solubilized Polymer I.

A 1% and 2% water solution of solubilized H_2S modified Polymer I was prepared by adding additional water to the solubilized Polymer I prepared as shown above. Sheets of bleached sulfite paper were treated as shown in the above examples so as to effect a 100% pick-up.

The sheets were pressed out on dry paper and allowed to dry at room temperature.

The resulting sheets had the appearance, feel and flexibility of the untreated paper, but demonstrated surprising improvement in wet strength, fold endurance, dimensional stability and resistance to loss of wet strength properties on prolonged exposure to water. The improvement in wet strength is shown in the following table:

Solution, Percent	Dry Strength	Wet Strength	Percent Strength Retention
1	14.4	6.8	47
2	17	8.2	48
Control	13.2	0.2	

Example VII

This example illustrates the improvement in properties obtained by treating bleached sulfite paper with solubilized Polyer J.

A 2% water solution of solubilized modified Polymer J prepared by adding additional water to the solubilized Polymer J prepared as shown above. Sheets of bleached sulfite paper were treated as shown in the above examples so as to effect a 100% pick-up. The sheets were pressed out on dry paper and allowed to dry at room temperature.

The resulting sheets had the appearance, feel and flexibility of the untreated paper, but demonstrated surprising improvement in wet strength, fold endurance, dimensional stability and resistance to loss of wet strength properties on prolonged exposure to water. The improvement in wet strength is shown in the following table:

Solution, Percent	Dry Strength	Wet Strength	Percent Strength Retention
2	12.8	5.2	41
Control	13.2	0.2	

Example VIII

To a water solution of paper pulp (1% sol.) was added aluminum sulfate to make a 1% solution and the mixture allowed to stand for 5 minutes. A sulfur dioxide solubilized polyacrolein having an intrinsic viscosity of 1.5 was added so that the resin solid was 1% of the pulp weight. This mixture was allowed to stand for 20 minutes at room temperature. A paper sheet was then pressed from this solution in the conventional manner and the sheet dried. The finished sheet showed a wet strength retention of 25%. A sheet of paper that had been dipped impregnated with the 1% solution of the sulfur dioxide solubilized polyacrolein had a wet strength retention of 30%.

Example IX

Example VIII is repeated using sulfur dioxide solubilized Polymers A to H. Related results are obtained.

Example X

Example VIII is repeated using a sulfur dioxide solubilized polyacrolein which has been previously neutralized. In this case, much higher wet strength retention values are obtained.

We claim as our invention:

1. A process for producing wet strength paper having improved properties which comprises adding an aqueous medium containing a water-solubilized polymer of acrolein to an aqueous suspension of paper pulp at the beater stage so as to form an aqueous medium containing 0.1% to 5% by weight of the water-solubilized polymer based on weight of the paper pulp, forming paper from the resulting product, and drying the formed paper, the said polymer of acrolein being obtained by polymerization through the carbon-to-carbon double bond of acrolein,

having an intrinsic viscosity of at least 0.5 and possessing when prepared at least 95% of the theoretical aldehyde function as determined by addition of hydroxylamine hydrochloride and titrating with Karl Fischer reagent the liberated water, the expression theoretical aldehyde as used above meaning one aldehyde group per unit of acrolein in the polymer.

2. A process as in claim 1 wherein the solubilized polymer is an SO_2-solubilized polyacrolein.

3. A process as in claim 1 wherein the solubilized polymer is a sodium bisulfite solubilized polyacrolein.

4. A process as in claim 1 wherein the polymer is one having an intrinsic viscosity of at least 0.6.

5. A process for preparing paper having improved wet strength which comprises impregnating already formed paper with an aqueous medium containing about .1% to 5% by weight of a water-solubilized polymer of acrolein and drying the treated paper, the said polymer of acrolein being obtained by polymerization through the carbon-to-carbon double bond of acrolein, having an intrinsic viscosity of at least 0.5 and possessing when prepared at least 95% of the theoretical aldehyde function as determined by addition of hydroxylamine hydrochloride and titrating with Karl Fischer reagent the liberated water, the expression theoretical aldehyde as used above meaning one aldehyde group per unit of acrolein in the polymer.

6. A process for producing paper having improved wet strength which comprises adding a wet strengthening amount of a water-solubilized polymer of acrolein to an aqueous medium of the paper pulp, forming paper from the resulting product and drying the formed paper, the said polymer of acrolein being obtained by polymerization through the carbon-to-carbon double bond of acrolein, having an intrinsic viscosity between 0.6 and 3.0 and possessing when prepared at least 95% of the theoretical aldehyde function as determined by addition of hydroxylamine hydrochloride and titrating the liberated water with Karl Fischer reagent, the expression theoretical aldehyde as used above meaning one aldehyde group per unit of acrolein in the polymer.

7. A process for preparing paper having improved wet strength which comprises applying to the paper an aqueous medium containing an effective wet strengthening amount of a water-solubilized polymer of an alpha, beta-ethylenically unsaturated aldehyde which polymer was obtained by addition polymerization through the carbon-to-carbon double bonds on the aldehyde and has an intrinsic viscosity of at least 0.5, and then drying the treated paper.

8. A process as in claim 7 wherein the water-solubilized polymer is a sodium bisulfite solubilized polyacrolein.

9. A process for preparing paper having improved wet strength which comprises padding the paper with an aqueous medium containing from 0.1% to 5% by weight of a sulfur dioxide adduct of a polymer of acrolein which polymer has been formed by addition polymerization at the double bond of acrolein and has an intrinsic viscosity of 0.5 to 3.0, and then drying the treated paper.

10. A process for producing wet strength paper having improved properties which comprises adding an aqueous medium containing an effective wet strengthening amount of a water-solubilized polymer of acrolein, to an aqueous suspension of the paper pulp, forming paper from the resulting product, and drying the formed paper, the said polymer of acrolein being obtained by polymerization through the carbon-to-carbon double bond of acrolein, having an intrinsic viscosity of at least 0.5 and possessing when prepared at least 95% of the theoretical aldehyde function as determined by addition of hydroxylamine hydrochloride and titrating with Karl Fischer reagent the liberated water, the expression theoretical aldehyde as used above meaning one aldehyde group per unit of acrolein in the polymer.

11. A process as in claim 10 wherein a polyvalent metal salt is added to the aqueous suspension of the paper pulp.

12. A process as in claim 10 wherein the water-solubilized polymer is a sodium bisulfite solubilized polyacrolein.

13. A paper impregnated with an aqueous medium containing an effective wet strengthening amount of a water solubilized polymer of an alpha, beta-ethylenically unsaturated aldehyde, which polymer has been formed by addition polymerization at the carbon-to-carbon double bond and has an intrinsic viscosity of at least 0.5.

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