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CELLULOSIC FIBROUS PRODUCTS AND METHODS OF MAKING THEM

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No Drawing. Continuation-in-part of applications Ser. No. 254,585, Jan. 29, 1963, and Ser. No. 280,702, May 15, 1963. This application Jan. 18, 1965, Ser. No. 426,416

Int. Cl. C08f 45/18

U.S. Cl. 260—17.4 9 Claims

ABSTRACT OF THE DISCLOSURE

This invention relates to improved cellulosic materials, like paper products. The invention is concerned with the use of a vinyl-imidazoline polymer in making improved cellulosic products and with methods for treating such materials. The invention also provides improved cellulosic products, like paper products, having increased dry strength, wet strength, tear strength, and other desirable properties. Another important embodiment of the invention provides for the deposition of an aqueous dispersion of a water-insoluble polymer in an aqueous system comprising fibrous cellulosic materials, such as paper pulp, suspended in a solution of the polymer used in this invention. The invention further provides for an aqueous composition comprising a dispersion of cellulosic fibers suspended in a solution of a water-soluble polymer. A further embodiment of the invention provides for a dispersion of cellulosic fibers and a water-insoluble polymer in a solution of a water-soluble polymeric material. The invention also provides for a process for beater deposition of a water-insoluble polymer on cellulosic products by means of the water-soluble polymer used in this invention.

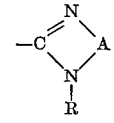
This application is a continuation-in-part of copending applications Ser. No. 280,702, filed May 15, 1963, now abandoned, and 254,585, filed Jan. 29, 1963, now U.S. Pat. 3,406,139, Oct. 15, 1968.

DESCRIPTION OF THE INVENTION

This invention relates to improved cellulosic materials, like paper products. The invention is concerned with the use of a polymer in making improved cellulosic products and with methods for treating such materials. The invention also provides improved cellulosic products, like paper products, having increased dry strength, wet strength, tear strength, and other desirable properties. Another important embodiment of the invention provides for the deposition of an aqueous dispersion of a water-insoluble polymer in an aqueous system comprising fibrous cellulosic materials, such as paper pulp, suspended in a solution of the polymer used in this invention. The invention further provides for an aqueous composition comprising a dispersion of cellulosic fibers suspended in a solution of a water-soluble polymer. A further embodiment of the invention provides for a dispersion of cellulosic fibers and a water-insoluble polymer in a solution of a water-soluble polymeric material. The invention also provides for a process for beater deposition of a water-insoluble polymer on cellulosic products by means of the water-soluble polymer used in this invention.

The preferred embodiments of the improved cellulosic

products of the invention are obtained by incorporating with the cellulosic fibers, especially an aqueous suspension thereof, to be used for making the products a water-soluble nitrogen-containing polymer, or a salt thereof, having a molecular weight of at least about 5,000 up to about 10,000,000 viscosity average, and having an exclusively carbon-atom "backbone" chain to which there are attached a plurality of nitrogenous rings of the formula



(I)

wherein:

A is an alkylene group having 2 to 3 carbon atoms, of which at least two extend in a chain between the adjoined N atoms, and

R is selected from the group consisting of H, (C_1–C_3)-alkyl groups, hydroxy-substituted (C_1–C_3)-alkyl groups, and groups of the formula —$(ANH)_xH$ wherein A is as defined above and x is an integer having a value of 1 to 4.

For convenience, the polymers used in the invention are hereinafter referred to as the PVI polymers. The polymers used in this invention are disclosed and claimed in the above-mentioned copending application Ser. No. 254,585, U.S. Pat. 3,406,139.

The specific manner in which the fibers are to be treated is not critical, as long as at one time or another during the process of the invention, there is provided an aqueous environment in which the cellulosic fibers are contacted with the PVI polymer and, if desired, with the water-insoluble polymer. When wet strength improvement in the paper products is desired, the cellulosic materials are treated, as by contacting, with the PVI polymer in an aqueous environment. When the PVI polymer is used as a deposition aid, such as a beater additive, the process generally involves suspending the desired amount of cellulosic materials in water and then, generally while mixing, adding thereto a solution of the PVI polymer. Then, a pigment paste or an aqueous dispersion of a polymer, preferably a water-insoluble "emulsion" polymer, is added to the pulp slurry containing the PVI polymer. The latter improves the pigment retention in making mineral-filled papers. The mineral filler or water-insoluble polymer is anchored to the cellulosic fibers by the PVI polymer and the fibers may be formed into a sheet on any suitable paper-making equipment. Generally, the cellulosic fibers are dispersed or suspended in water, preferably with the aid of agitation. The consistency of the paper pulp may be as low as 0.01% or as high as 10% by weight of the dry fiber on the weight of the water. Perferably, the consistency is between 1% and 4%.

One preferred embodiment of the invention provides for an improved and accelerated deposition of a water-insoluble polymer on the paper stock. For this purpose, the preferred polymers have viscosity average molecular weights of about 25,000 to about 50,000 in their free amine form. The process provides for a more efficient and better retention, as well as a more uniform distribution of the water-insoluble polymer on the fibers and on the sheets formed from such fibers. The uniform deposition of pulp additive, such as filler, or water-insoluble emulsion polymer, that is obtained by the present invention is especial-

ly important. The PVI polymer is adsorbed on the fibers and then the pulp additive is not simply coagulated in zones of the pulp slurry unoccupied by the fibers, but is deposited on the fibers in proximity to the PVI polymer carried thereon. This uniform deposition may in some cases require agitation only for periods of less than 5 minutes even when the agitation is gentle. On the other hand as much as 30 minutes or an hour or more of gentle to moderate agitation may be needed. Since the paper-making stock frequently resides for one to two hours in certain parts of normal paper-making equipment, such as in the machine chest or in the beater, the process of the present invention is readily adaptable to such equipment. The system of the invention, moreover, minimizes the losses of the water-insoluble polymer. The treatment of the paper pulp is accomplished faster; greater amounts of polymer may be deposited onto the paper pulp within a certain time and a greater variety of water-insoluble polymers, which heretofore have presented serious difficulties, may now be used in the treatment of paper pulp. As a result, the treated cellulosic products of the invention have an improved combination of properties. They demonstrate good sheet formation, improved tensile and tear strength. Moreover, impact strength and water-resistance of molded or pressed paper products can be improved, too.

The PVI polymer may be added as a powder in the dry form or as a water solution thereof, whichever is most convenient. The smallest amount of PVI polymer that may be used is that which brings about an improvement in the paper product or in the deposition of the filler or insoluble polymer on the paper pulp. The maximum amount, preferably, should be short of that which will bring about the coagulation of the paper pulp. Generally, the amount of PVI polymer ranges from 0.05 to 50%, based on the dry weight of the fiber. As a deposition aid, the PVI polymer generally is used in an amount of 0.05 to 5%, and preferably from 0.25 to 2%, by weight, based on the weight of the fiber to be treated. For use as a wet strength resin, the preferred amount is 0.5% to 3% based on pulp. The PVI polymer may be added all at once or gradually to the aqueous system of the dispersed cellulosic fibers. For optimum results, the PVI polymer is thoroughly contacted with the cellulosic fibers. This is generally effectuated by mixing, such as by gentle agitation.

In the aforesaid preferred embodiment, the water-insoluble polymer is generally used in amounts ranging from 10% to 40% or even up to 60% by weight, based on the weight of the cellulosic fibers.

The deposition of the water-insoluble polymers may be carried out with the aqueous fiber system at a pH not exceeding that at which the fibers will tend to coagulate, generally a pH of 3 to 12; 4 to 11 being generally more satisfactory. One of the distinctive advantages of the present invention is that the PVI polymer is quite effective in depositing, on the fibers in aqueous suspension, water-insoluble polymers from dispersions thereof prepared with non-ionic dispersing and emulsifying agents. While these non-ionic dispersons can be deposited at any pH, they are preferably deposited at a pH of 4 to 7. When the PVI polymer is principally used to treat the paper fibers to impart wet strength, the treatment is favored on the alkaline side, for maximum efficiency, as in the range of 7 to 10, or better at 7 to 9. An acidic pH may be reached by the addition of any suitable acidic material, such as strong mineral acids, such as sulfuric, hydrochloric, or phosphoric acids, or by the incorporation of acidic salts, such as sodium or potassium aluminum sulfate or the corresponding chrome alums, sodium zirconium silicate, and various acidic materials. For adjustment of the pH to the alkaline side, any convenient basic material may be used as the hydroxides of the alkaline earth metals and alkali metals, like the hydroxides of sodium, potassium, and the like.

The PVI polymer may also serve as an anchoring agent for the retention of various pulp additives other than the water-insoluble polymers of the preferred embodiment. A large variety of such additives or fillers is used in the making of paper. These materials may serve as pigments or colorants; they generally impart opacity and brightness to the paper. Typical of such fillers are clays, titanium dioxide, talc, and the like. They may be used in amounts from 0.5% to 20% by weight, based on the weight of the dry fiber. Such fillers and various methods of incorporating them in the paper by addition to the paper pulp are disclosed in U.S. Pat. 2,838,397 the disclosure of which is herein incorporated by reference.

It is preferred to add the polymers after all mechanical refining of the fibers is completed. The fiber supsenion and the addition of the polymers are generally performed at a convenient location after the processing of the paper pulp, such as in the machine chest, fan pump, or the head box.

Any fibrous cellulosic material capable of adsorbing the water-insoluble polymer used in this invention from an aqueous dispersion may be coated or impregnated by the process of the invention. A wide variety of fibrous cellulosic materials can be, accordingly, used. Such cellulosic materials are disclosed in U.S. Pat. No. 2,601,598, column 7, which is hereby incorporated by reference, and U.S. Pat. No. 2,910,399, column 3. Of particular interest in this invention is the treatment of cellulosic fibers in the form of bleached or unbleached wood pulps, including sulfite, kraft, soda, semi-chemical and ground wood pulps, as well as rag pulp, rope pulp, jute pulp, and the like. The pulp may be unbeaten, highly beaten, or lightly beaten before the treatment with the polymers.

When the PVI polymer is used as a deposition aid, any water-insoluble polymer may be deposited on and anchored to the cellulosic fibers. A desirable group of polymers are the homopolymers and copolymers of esters of acrylic or methacrylic acid, which acids may be represented by the formula

$$CH_2=\underset{\displaystyle COOH}{\overset{\displaystyle |}{C}}-(CH_2)_{n-1}H$$

wherein n is an integer having a value of 1 to 2.

Typical esters are methyl acrylate, ethyl acrylate, propyl acrylate, isopropyl acrylate, butyl acrylate, isobutyl acrylate, sec-butyl acrylate, amyl acrylate, isoamyl acrylate, hexyl acrylate, 2-ethylhexyl acrylate, octyl acrylate, 3,5,5-trimethylhexyl acrylate, decyl acrylate, dodecyl acrylate, cetyl acrylate, octadecyl acrylate, octadecenyl acrylate, n-amyl methacrylate, sec-amyl methacrylate, hexyl methacrylate, 2-ethyl-butyl methacrylate, octyl methacrylate, 3,5,5-trimethylhexyl methacrylate, decyl methacrylate, dodecyl methacrylate, octadecyl methacrylate, and butoxyethyl acrylate or methacrylate. Other useful esters are those of acrylic and methacrylic acids and such typical alkenols as allyl, methallyl, undecenyl; typical alicyclic alcohols, such as cyclopentyl, methylcyclohexyl, trimethylcyclohexyl, or terpenyl; typical aralkanols, such as benzyl and phenylethyl; typical ester-forming phenols, such as phenyl and all other alcohol residues. Additional polymerizable monovinylidene monomers that are also useful are the following: t-amyl methacrylate, t-butyl or t-amyl acrylate and cyclohexylbenzyl.

Other useful linear addition polymers include the water-insoluble copolymers or homopolymers of the following: the cyanoethyl and aminoethyl esters of the above acids; esters of itaconic acid and the alcohols used in the above esters, esters from maleic, fumaric or citraconic acids, and the alcohols used in the above esters; vinyl esters of carboxylic acids, such as acetic, propionic, butyric, and the like; vinyloxyalkyl esters, such as vinyloxyethyl acetate, etc.; vinyl ethers, such as ethyl vinyl ether, butyl vinyl ether, octyl vinyl ether, hydroxyethyl vinyl ether, vinyloxyethoxyethanol, vinyloxypropoxyethanol; methacrylonitrile or acrylonitrile; acrylamide, or methacrylamide, and N-substituted amides, such as N-dialkyl acrylamides, like N-dimethyl, -diethyl, -dipropyl, -dibutyl, -di-

amyl, -dihexyl, -dioctyl acrylamides, N-methyl methacrylamide, N-(β-dimethylamino)ethylacrylamide, and N-(β-dimethylamino)ethyl methacrylamide; vinyl chloride, vinyl bromide, vinylidene chloride, vinylidene fluoride, vinylidene cyanide, 1-chloro-1-fluoroethylene, ethylene, styrene. These monomers may also be copolymerized with small amounts (from about 0.5% to 7.5% by weight of the total monomer mixture) of an acid, such as methacrylic acid, acrylic acid, itaconic acid, maleic acid, and fumaric acid, or of hydroxyl-containing acrylates, methacrylates, or the corresponding amides, such as β-hydroxyethyl acrylate, β-hydroxyethyl methacrylate, N-β-hydroxyethyl acrylamide, N-β-hydroxyethyl methacrylamide, and others disclosed in U.S. Pat. No. 2,923,653, column 1, which is incorporated herein by reference or of other monomers, such as N-methylolacrylamide, N-methylolmethacrylamide, and mixtures thereof. Other useful polymers are the elastomeric isoprene polymers, neoprene or butadiene polymers and copolymers, such as with acrylonitrile and natural latices; or other polymers as disclosed by U.S. Pat. No. 2,601,598, column 6.

If desired, in the dispersion system of the invention, there may be used an emulsifier or a dispersing agent. For instance, there may be used a non-ionic emulsifier, such as an alkylphenoxypolyethoxyethanol having an alkyl group of about 7 to 18 carbon atoms and 6 to 60 or more oxyethylene units, such as heptylphenoxypolyethoxyethanols, octylphenoxypolyethoxyethanols, and other, such as those disclosed in U.S. Pat. No. 2,765,229, column 5. If anionic emulsifiers are desired, there may be used soaps of higher fatty acids having 12 to 18 carbon atoms, namely those of sodium, potassium, ammonium, or amines, and others, such as those disclosed in U.S. Pat. No. 2,910,399, column 3.

After the fiber slurry is sheeted on a foraminous forming surface, such as on the endless wire screen of conventional paper-making machinery, the sheet may be pressed before and after drying to the extent needed to produce the final density desired in the sheet. The invention may be used to produce any type of paper including paperboard. The paper products of the invention are characterized by improved tensile strength, tear strength, bulk drape, wet and dry surfaces, and internal fiber bonding, stiffness and flexural strength, and water resistance. When the PVI polymers are used to impart wet strength to the cellulosic products, it is desirable to age the treated sheet one to thirty days at room temperature to develop maximum wet strength or by an accelerated cure at temperatures of 100° to 150° C. for periods of three to fifteen minutes, the time being selected in inverse relation to the temperature.

To assist those skilled in the art to practice the present invention, the following modes of operation are suggested by way of illustration, parts and percentages being by weight and the temperatures in ° C. unless otherwise specifically noted.

(1) To 1000 parts of a lightly beaten bleached sulfite pulp having a 2% consistency and a Canadian Freeness of 610 ml., sulfuric acid is added to adjust the pH to 5. Then 2 parts of a 5% solution of a bisulfate salt of a 2-vinyl-2-imidazoline polymer (obtained by reaction of excess ethylenediamine on a polyacrylonitrile having a molecular weight of about 18,000 viscosity average) is added to the pulp which is gently agitated for about five minutes. The resulting pulp is sheeted and dried for 2 minutes at 200° F. Whereas a sheet formed from this pulp without the PVI polymer has a dry tensile strength of 29 lbs./in. width per 100 pounds basis weight (basis weight is the weight of 500 sheets each of 2 ft. by 3 ft. dimensions) whereas the sheet treated with the PVI polymer has a dry tensile of 33 lbs./in. width per 100 pounds basis weight. Similarly the wet strengths are 0.1 and 2.3 lbs. per inch width per 100 pounds basis weight for untreated and treated sheets respectively.

(2) Similar improvement in wet strength is obtained when (1) is repeated using a corresponding amount of each of the following PVI polymers in place of that used in (1):

(a) The sodium bisulfate salt of a polymer of 2-isopropenyl-imidazoline-2 (obtained by reaction of excess ethylenediamine on a polymethacrylonitrile having a viscosity average molecular weight of about 15,000 so that the nitrile groups are converted to the imidazoline-2 groups).

(b) The free base form of a polymer of 2-vinyl-3,4,5,6-tetrahydropyrimidine (obtained by the reaction of excess trimethylenediamine on a polyacrylonitrile having a viscosity average molecular weight of about 30,000 so that the nitrile groups are converted to tetrahydropyrimidine groups).

(c) The hydrochloric acid salt of a polymer of 2-vinyl-4 (or 5)-methyl-2-imidazoline (obtained by the reaction of excess 1,2-diaminopropane on a polyacrylonitrile having a viscosity average molecular weight of about 15,000 so that the nitrile groups are replaced by substituted imidazoline groups).

(3) A bleached, moderately beaten sulfite paper pulp slurry having a pH of about 5, a 2% consistency, and a Canadian Standard Freeness of 460 ml. is prepared. To a portion of the slurry, there is admixed a certain proportion by weight, based on the weight of the fibers in the pulp, of a PVI polymer for approximately 5 minutes so that the cationic PVI polymer is adsorbed onto the pulp fibers. There is then added a certain proportion by weight of an aqueous dispersion of an emulsion polymer, the proportion of emulsion polymer solids being based on the weight of the fibers of the pulp and slow mixing is continued until deposition of the polymer on the fiber is substantially complete.

The following Table I summarizes the results for various emulsion polymers and PVI polymers. The percentages of these polymers are based on weight of fiber in the pulp. The PVI polymers used include those of (1) above and of (2)(a), (2)(b), and (2)(c) and these are so designated. In addition, analogous PVI polymers of higher molecular weights are used as follows:

(1)(d) A homopolymer of 2-vinyl-2-imidazoline obtained from a polyacrylonitrile having a viscosity average molecular weight of about 1,500,000.

(1)(e) A copolymer of 2-vinyl-2-imidazoline obtained from a copolymer of 50 mole percent acrylonitrile and 50 mole percent methyl acrylate having a molecular weight of about 900,000 viscosity average.

(2)(d) A homopolymer of 2-isopropenyl-2-imidazoline obtained from a polyacrylonitrile having a molecular weight of about one million viscosity average.

(2)(e) A homopolymer of 2-vinyl-3,4,5,6-tetrahydropyrimidine having a viscosity average molecular weight of 600,000.

(2)(f) A homopolymer of 2-vinyl-4(or 5)-methyl-2-imidazoline obtained from a polyacrylonitrile having a viscosity average molecular weight of 1.7 million.

In the table the monomer composition of the emulsion polymers is abbreviated as follows:

EA represents ethyl acrylate
MA represents methyl acrylate
MMA represents methyl methacrylate
Am represents acrylamide
MIAm represents N-methylolacrylamide
MAm represents methacrylamide
S represents styrene
VCl_2 represents vinylidene chloride
MAA represents methacrylic acid
IA represents itaconic acid
VA represents vinyl acetate

The emulsion polymers are prepared with non-ionic

emulsifiers, such as tert-octylphenoxypoly(40)ethoxyethanol, except in those instances marked with an asterisk wherein sodium lauryl sulfate is used as the emulsifier.

TABLE I

Run	PVI	Percent PVI	Emulsion polymer composition (wt. percent monomers)	Percent emulsion polymer	Percent Transmittance of filtrate at time (in minutes)
1	(1)	0.5	70 EA/30 AN	30	91 (30)
2	(1)(d)	0.5	95 EA/2.5 MlAm/2.5 Am	30	92 (10)
3	(1)(e)	0.5	95 EA/2.5 MlAm/2.5 Am	30	95 (10)
4	(1)	0.5	95 EA/2.5 MlAm/2.5 Am*	30	98 (30)
5	(2)(a)	0.5	95 EA/2.5 MlAm/2.5 Am*	30	100 (30)
6	(2)(b)	2	68 EA/30 S/2 MAA	40	97 (5)
7	(2)(c)	0.5	65 EA/35 VCl_2	10	100 (10)
8	(1)(f)	1	68 EA/30 MMA/2 IA	60	98 (20)
9	(2)(d)	1	97 MA/3 IA	10	100 (25)
10	(2)(e)	1	100 VA	50	96 (20)
11	(2)(f)	1	72 EA/23 MMA/5 MAm	40	97 (30)
12			65 EA/35 VCl_2	10	44 (10)

(4) To 1000 parts of a moderately beaten bleached sulfite pulp having a 1% consistency, a pH of 4, and a Canadian Freeness of 460 ml., there is added a 5% solution of sodium hydroxide to adjust the pH of 9.0. Then one part of a 5% aqueous solution of the PVI polymer used in (1) above except that it is in free base form is added to the pulp and mixed therewith for ten minutes. The pulp is sheeted and dried at 200° F. for 2 minutes. The sheet has a wet tensile strength of 4.6 lbs. per inch width per 100 pounds basis weight whereas the corresponding value for a sheet formed from the untreated pulp is 0.2. After 28 days the wet strength rises to 5.4 lbs./inch width.

(5) The process of (3) is repeated using a moderately beaten bleached sulfite pulp having a pH of 5, 2% consistency, and a Canadian Freeness of 610 ml. Instead of determining transmitance, the treated pulp is sheeted, dried at 200° F. for 2 minutes, and then the edge tear factor is determined. The edge tear is determined according to TAPPI Standard Test No. T-470 and it is in pound units. The factor is equal to 100 times the edge tear (in pounds) divided by the basis weight of the paper tested. Table II summarizes the results.

TABLE II

Run	PVI	Percent PVI	Emulsion polymer composition (wt. % monomers)	Percent emulsion polymer	Edge tear factor
13	(1)	0.5	89 EA/10 MMA/1 MlAm.*	30	34
14	(1)	0.5	89 EA/10 MMA/1 MlAm.*	15	21
15	(1)	0.5	None		11
16					9

(6)(a) To 1000 parts of a moderately beaten bleached sulfite pulp (475 ml. Canadian Freeness) having a 1% consistency there is added, with agitation, 0.5 part of pigment-grade titanium dioxide and 0.2 part of papermaker's alum. It is then diluted to 0.04% consistency, adjusted to a pH of 4.5 with sulfuric acid, and then 0.01 part of the bisulfate salt of the poly(2-vinyl-2-imidazoline) referred to hereinbefore ((1)(d) above) is mixed thoroughly into the pulp/pigment slurry. The pulp is sheeted. The pigment retention is determined by determining the amount of ash after burning the sheet. In addition, the effectiveness of the treating system to opacify the sheet is determined by conventional tests involving measuring the "oiled opacity" after applying mineral oil to the sheet, the "TAPPI dry opacity" and the "light-scattering coefficient" of the pigment in the paper. This procedure is repeated without using a PVI polymer. It is also repeated using instead of the PVI polymer, each of two previously recommended acrylamide polymers, which, in Table III showing the results of these runs, are identified as Polymer A and Polymer B respectively.

TABLE III

Polymeric pigment-retention aid	Oiled opacity	TAPPI Dry opacity	Scattering coefficient	Percent ash	Percent pigment retention
None	17	72	75.2	1.10	23.1
(1)(d) supra	37	77	59.0	3.07	64.5
Polymer A	17	72	27.3	2.52	52.9
Polymer B	12	71	36.3	1.91	40.1

NOTE.—Dry opacity is determined by TAPPI Test No. T-425 using a blue filter (450–500 millimicrons wavelength).

The determination of scattering coefficient is described in T–425 above and in Paper Trade Journal, vol. 101, No. 5, August 1955, pp. 58–61 (D. Judd).

Oiled opacity is measured after soaking the sheet 30 minutes in mineral oil (Atreol 9) and then following T–425 above except that instead of the blue filter, a green filter (500–575 millimicrons wavelengths) is used.

(b) Similar results are obtained when the PVI polymer of part (a) hereof is replaced with a respective one of the other specific PVI polymers hereinbefore designated (1)(e), (2)(d), (2)(e), and (2)(f).

(7) A bleached sulfite pulp (1000 parts) beaten to 465 ml. Canadian Standard Freeness is adjusted to a 2% consistency. It is then treated by one of the following procedures:

(a) A high molecular weight poly(2-vinyl-2-imidazoline) (molecular weight, approximately one and a half million) (0.5 part) is added to, and mixed thoroughly within, the pulp slurry at a pH of 5, followed by 0.2 part of formaldehyde to give the formaldehyde condensation product of the PVI polymer. The paper is sheeted and dried at 200° F. for 2 minutes. After ageing the paper for 30 days, it is found to have a wet tensile strength of 6.1 lbs./inch width.

(b) The condensation product of 0.5 part of the bisulfate salt of the PVI polymer of (1) hereinabove and 0.2 part of formaldehyde is added to the pulp slurry. After drying as in part (a) hereof and 30 days of ageing, the wet tensile strength is 5.0 lbs./inch.

(8) To 10,000 parts of a moderately beaten blend of bleached softwood and hardwood kraft pulp of 1% consistency there are added 15 parts of a pigment mixture (85% calcium carbonate and 15% clay (Ultra White 90)) and 0.2 part of octadecyl ketene dimer (a paper sizing agent useful in alkaline systems). The pulp is then diluted to 0.1% consistency. Its pH is about 7.8. The pulp is divided into five portions, one of which is diluted to a consistency of 0.04% with water at a pH of 7.8, formed into a sheet on a 100-mesh wire screen in a sheet-forming mold. The sheet is wet-pressed between

felts, and dried at 200° F. for 2 minutes to a moisture content of about 6%. The pigmented sheet has a basis weight of about 54 lbs. (i.e. 54 lbs./3300 sq. ft.). Into the other four portions there are mixed small amounts (0.05%, 0.01%, or 0.2% on the fiber weight) of a PVI polymer, either that of (1) above or that designated (1)(d) above. These portions are then diluted to 0.04% consistency, formed into sheets and dried in the same way as the first. In addition a control sheet is formed from the same pulp but without pigment, ketene dimer sizing, and PVI polymer. The ash, pigment retention, oiled opacity and dry opacity of all sheets are measured. In addition, the sizing effect is measured by determining the time required for reduction of the reflectance (from 100% to 75%) of the underside of the sheet immediately beneath 4 cc. of a blue-black ink (Sheaffer's No. 232) held in place on the sheet with a 1-inch diameter ring. The following Table IV summaries the results obtained.

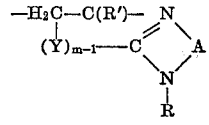
TABLE IV

Pulp portion	PVI polymer percent on fiber	Oiled opacity [1]	TAPPI dry opacity [1]	Percent ash	Percent pigment retention [2]	Sizing [3] (sec.)
Control		12	89	0.37		
1		16	90	2.04	22.7	03
2	0.05 (1)	19	94	4.74	59.4	944
3	0.1 (1)	19	95	4.64	57.8	1,200+
4	0.1 (1)(d)	22	95	5.88	75.0	1,200+
5	0.2 (1)(d)	21	96	6.05	77.0	1,200+

[1] Higher values indicate higher opacity.
[2] Pigment blend contains 60.85% ash.
[3] Greater times indicate greater sizing effect.

Instead of the PVI polymers having recurring units of Formula I hereinabove, there may be used any of the PVI polymers of the aforesaid prior applications which have recurring units of the Formula I as defined in U.S. Patent 3,406,139 or Ser. No. 280,702 and which are sufficiently water-soluble to dissolve the necessary amount, such as from 0.05 to 5%, of the PVI polymer in the aqueous fibrous suspension, for the treatment of the fibers therein.

In the water soluble polymer, the nitrogenous rings of Formula I may be connected directly to carbon atoms in the polymer chain or they may be connected through a phenylene group or through an ester or amide linkage. Thus, the typical polymerized unit of the polymers used in carrying out the present invention may in most cases be represented generically by the following formula

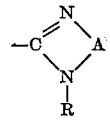


(II)

wherein:

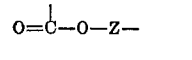
A and R are as defined hereinbefore,

R′ is selected from the group consisting of H and (C_1–C_2)-alkyl, phenyl, C_7-alkaryl, and

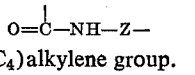


m is an integer having a value of 1 to 2, and

Y is selected from the group consisting of phenylene,



and

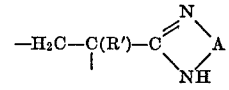


wherein Z is a (C_1–C_4)alkylene group.

The preferred polymers are those in which each unit of Formula II contains only 5 to 8 carbon atoms, and optimum results are obtained with polymers in which such units contain only 5 carbon atoms, that is units of 2-vinyl-imidazoline-2.

To assure water-dispersibility of the polymers, the number of carbon atoms in each unit of Formula II should not exceed 12 carbon atoms. In general, the polymers used in accordance with the present invention contain at least 50 mole percent of units of Formula II and preferably about 90 to 100 mole percent thereof.

Preferred polymers are those containing 50 to 100 mole percent of units of the formula

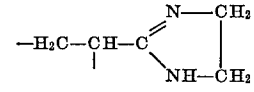


(III)

wherein:

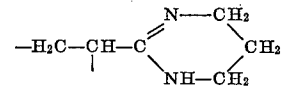
R′ is selected from the group consisting of H and CH_3 and

A is a (C_2–C_3)-alkylene group having at least 2 carbon atoms extending in a chain between adjoined N atoms. Preferred species include the polymers containing 50 to 100 mole percent of units of the formula



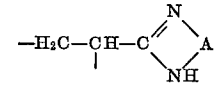
(IV)

which contain 2-imidazoline groups, or of the formula



(V)

which contain 3,4,5,6-tetrahydropyrimidine groups, or of the formula



(VI)

in which A is the propylene group

(—CH_2—CH(CH_3)—)

and which contain C-methyl-substituted imidazoline-2 groups, or more specifically 4(or 5)-methyl-2-imidazoline groups.

The method of preparation of the polymeric deposition aids of the present invention, is not per se claimed as part of the present invention. The disclosure of U.S. Pat. 3,406,139 in regard to the making of three polymers is incorporated herein by reference.

It is essential that the polymer salts to be used as deposition aids be of water-soluble character. This term is meant to include both true solubility as well as that type of dispersibility in water characteristic of high molecular weight molecules, such as result in the so-called colloidal solutions of dispersions. The most efficient polymer salts are generally those having the highest hydrophilicity.

The acids that may be used to convert the polymer containing units of Formula II to the salt form may be

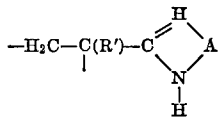
any organic or inorganic acid or acid salt. The acid is preferably a strong acid. Examples include:

hydrochloric	p-toluene sulfonic
hydrobromic	phosphoric
hydroiodic	sodium acid phosphates
sulfuric	nitric
ammonium sulfate	acetic
sodium bisulfate	oxalic
potassium bisulfate	propionic
monomethyl hydrogen sulfate	tartaric
	citric
sulfurous	sulfamic
sodium bisulfite	glycolic
sulfonic	diglycolic
benzene sulfonic	ethylenediaminetetraacetic

The term salt herein is intended to embrace not only the ordinary salts formed with acids, such as those just mentioned, but also such quaternary ammonium salts formed by quaternizing the NR groups of one or more of the units of Formula II in the polymer as are still water-soluble. Alkylating agents which do not detrimentally affect the water-solubility of the polymers are preferably used, such as methyl chloride, methyl bromide, ethyl chloride, dimethyl sulfate, dimethyl sulfite, and dimethyl phosphate. The alkylation may be effected by heating a mixture of the polymer and the alkylating agent in a suitable solvent and, if necessary, under pressure (as in the case of methyl bromide) at a temperature of 40 to 130° C., such as at reflux at the pressure used. Suitable solvents include alcohols, such as absolute ethanol, and isopropanol, acetonitrile, dimethylformamide, and nitropropane. The mixture may be heated for a half hour or more depending on the temperature and the extent of alkylation desired.

We claim:

1. A composition consisting essentially of a suspension of cellulosic fibers in water containing dissolved therein from 0.05 to 50% by weight, based on the weight of said fibers of a water-soluble addition polymer, or a water-soluble salt thereof, of monoethylenically unsaturated molecules, at least 50 mole percent of said polymer consisting essentially of repeating units of the formula



wherein A is an alkylene group having 2 to 3 carbon atoms, of which at least two extend in a chain between the adjoined N atoms, and R′ is selected from the group consisting of H and methyl.

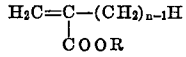
2. The composition of claim 1 in which the polymer is a homopolymer.

3. A composition as defined in claim 1 in which the consistency of the suspension is from 0.01 to 10% by weight of the dry fiber on the weight of the water.

4. A composition as defined in claim 3 which also comprises, dispersed therein, up to 60% by weight, based on the weight of fibers, of a water-insoluble organic polymer of ethylenically unsaturated molecules.

5. A composition as defined in claim 3 which also comprises, dispersed therein, 0.5 to 20% by weight, based on the weight of fibres, of a water-insoluble filler.

6. A composition according to claim 4 in which the water-insoluble polymer is a polymer of monoethylenically unsaturated molecules comprising at least one ester of the formula



wherein *n* is an integer having a value of 1 to 2, and R is an alkyl group.

7. A composition according to claim 6 in which the water-insoluble polymer is a copolymer of at least one ester as defined with an amide of an acid selected from the group consisting of acrylic and methacrylic acids.

8. A composition according to claim 6 in which the water-insoluble polymer is a copolymer of ethyl acrylate and at least one other monoethylenically unsaturated monomer.

9. A composition according to claim 6 in which the water-insoluble polymer is a copolymer of methyl methacrylate and at least one other monoethylenically unsaturated monomer.

References Cited

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3,288,707	11/1966	Hurwitz et al.	
3,300,406	1/1967	Pollio.	

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U.S. Cl. X.R.

260—29.6, 85.5, 88.7, 89.5