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2,910,399

PROCESS FOR MAKING CELLULOSE FIBROUS SHEET

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This invention relates to a process for deposition of polymeric materials on fibers and is particularly concerned with the deposition of an aqueous dispersion of a water-insoluble polymer on fibers, such as paper fibers, suspended in the aqueous system by means of polyvalent metal salts, such as alum.

Heretofore, when alum or like polyvalent metal salt has been used to coagulate a dispersed polymer on fibers within an aqueous suspension thereof, the alum has generally been added after the introduction of the dispersed polymer into the fiber suspension or slurry. Because of the impossibility of getting the alum to become adsorbed on the fiber surfaces before coagulation of the polymer is effected, the polymer particles have the opportunity to form numerous large aggregates in the aqueous medium before adsorption occurs on a fiber. The result is a so-called irregular deposition of non-uniform character sometimes called a "grape-bunch" effect. A similar problem arises when the alum is dissolved and uniformly distributed through the fiber suspension before adding the polymer dispersion. Attempts have been made to limit the amount of alum to that and only that which can be completely adsorbed by the fibers so that the polymer particles can be only deposited or coagulated on the fiber surfaces. However, this control of the amount of alum requires extreme care and it has been found that insufficient alum can be adsorbed exclusively on the fiber surfaces while suspended in the aqueous system to provide the necessary coagulating power to completely deposit the dispersed polymer on the fibers unless relatively small proportions of polymer (on weight of fiber) are used. Hence, the general practice has been to add additional alum after the introduction of the polymer dispersion to exhaust the polymer onto the fibers. It has also been suggested in U.S. Patent 2,375,245 to precipitate a metal hydrate, such as aluminum hydrate, on the fiber to aid the subsequent deposition of a natural or synthetic rubber. It has been found, however, that the action of the hydrate on the polymer dispersion is relatively feeble and sheets obtained by this procedure frequently show little, if any, of such benefit as is normally expected of polymer deposition on the fiber in the making of fibrous sheets, especially paper or paperboard. Because of the difficulties encountered with alum and the like, there have been many suggestions for replacing the alum at least partly with organic polymeric materials having a multiplicity of cationic charges, but while these coagulants are highly effective, they are nevertheless comparatively expensive.

In accordance with the present invention, an improved process is provided for the use of a polyvalent metal salt, such as alum, for the deposition of aqueous polymer dispersions on fibers in aqueous suspension. The process provides better retention and more uniform distribution of polymer on the fibers and sheets formed from such fibers are more uniform and have better physical properties. The process of the present invention involves the preliminary treatment of the fibers with an aqueous solution containing at least 10% and preferably at least

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15% of the polyvalent metal salt. If desired, the concentration of the salt may be at the saturation point in the aqueous medium in which the fibers are suspended for the treatment. After thorough mixing and intermingling of the fibers in the solution of the polyvalent metal salt, the excess solution is removed, such as by straining or filtering the slurry or suspension through a porous body, such as through a conventional wire screen used in the paper-making industry, which may be assisted by the conventional suction box.

The fibers are then rinsed rapidly to remove any loosely held polyvalent metal salt carried on the surface of the fibers. Rinsing is effected with water, either soft or hard, but preferably the former, at any convenient temperature from about 15° C. to 40° C. This may be simply accomplished by spraying the water on the fibers while they are supported on a conventional paper-making screen or other foraminous or porous support. Removal of the rinse liquid may involve simple draining or the latter may be aided by suction.

After rinsing, the fibers are quickly dispersed, or suspended in water quickly, preferably with the aid of agitation. The consistency may be as low as 0.1% or as high as 6% by weight of fiber on the weight of water. Preferably, the consistency is between 1% and 3%. As soon as the fibers are well-distributed in the liquid, the polymer dispersion is added and mixed into the fiber suspension in the proportion desired. This may be from about 1% by weight of polymer to 150% by weight thereof on the weight of the fiber depending on the properties desired in the ultimate fibrous product. The benefits obtained by the procedure of the present invention are particularly valuable when the polymer is used in higher proportions from 10% and especially from 25% up to 150% on the weight of fiber. The addition is preferably accompanied by suitable mixing action, such as by gentle agitation.

The prompt addition of the polymer dispersion to the freshly dispersed fibers serves to bring the polymer particles into contact with the polyvalent metal ions on the fiber or in close proximity to its surface. Rapid preparation of the fiber suspension and reasonably prompt mixing of the polymer dispersion into the freshly prepared fiber suspension precludes the liberation of polyvalent metal ions into the body of the liquid in sufficient concentration to cause any appreciable aggregation of coagulated polymer particles therein apart from the fibers. The polymer particles are deposited substantially uniformly and completely on the fiber surfaces.

After deposition of the polymer particles is complete, the fibers may be formed into a sheet on any suitable equipment, such as on any of the various types of paper-making equipment including laboratory types having sieves or screens for making handsheets as well as commercial machines, such as those using the typical Fourdrinier wire screen or perforated rotating cylinders.

As the polyvalent metal salts, there may be used any water-soluble salt of a trivalent or tetravalent metal of groups III, IV, V, and VI of the periodic table. Examples include the water-soluble sulfates, chlorides, nitrates, and so on of aluminum, titanium, zirconium, tin, vanadium, antimony, chromium, molybdenum. Simple salts may be used such as aluminum chloride, stannic chloride, or aluminum sulfate. Basic salts may be used, such as molybdenum oxytrichloride, vanadyl sulfate, zirconium oxychloride, or basic zirconium sulfate. Also, basic aluminum sulfate, $\text{Al}(\text{OH})\text{SO}_4$, used in the paper industry and frequently referred to as papermaker's alum, may be used. Also double salts, such as sodium zirconium silicate, or the alums, such as sodium or potassium aluminum sulfate or the corresponding chrome alums are suitable. From the standpoint of inexpensiveness,

availability, reliability and convenience, the common potassium alum or papermaker's alum is preferred.

In producing fibrous products in accordance with my invention any suitable type of fibrous material may be employed and when producing a light weight sheet part or all of the fibrous material used is generally vegetable fiber, such as news fiber. However, cotton fibers, cotton linters, wool and wood or rag fibers as well as asbestos or mineral fibers may be employed. The invention is particularly valuable for the preparation of modified paper or paperboard sheets from cellulosic fibers in the form of bleached or unbleached wood pulps, including sulfite, kraft, soda, semichemical, and groundwood 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.

The polymer dispersion used may comprise any water-insoluble linear addition polymer either of neutral character or of anionic character, that is, it may, but need not, contain carboxylic or sulfonic acid groups either in acid form or in the form of a salt of ammonium, of an alkali metal, such as sodium, potassium, or lithium, or of a water-soluble amine, such as trimethylamine, an alkylamine, such as monoethanolamine, di-, or triethanolamine, morpholine, and so on. The polymer may be any homopolymer or copolymer preferably obtained by emulsion polymerization of one or more of the following monoethylenically unsaturated monomers: esters of acrylic acid or methacrylic acid and monohydric alcohols such as methyl, ethyl, butyl, octyl, dodecyl, cyclohexyl, cyanoethyl, aminoethyl, and the like; esters of itaconic acid and the above alcohols; esters from maleic, fumaric or citraconic acids, and the above alcohols; vinyl esters of carboxylic acids such as acetic, propionic, butyric, and the like; vinyloxyalkyl esters such as vinyl-oxyethyl 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 of these types; 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, fumaric acid, and so on.

In the emulsion copolymerization either an anionic or a non-ionic emulsifying or dispersing agent, or a mixture thereof may be used. When the polymer lacks anionic groups such as carboxyl or sulfonic acid groups in acid or salt form, it is generally preferable, but not essential, that an anionic emulsifier be used as the entire dispersing agent or as a substantial part of it or that the amount of non-ionic emulsifier that is used as the sole emulsifier is limited so that the polymer dispersion has limited stability toward polyvalent metal ions.

Examples of anionic emulsifiers that may be used include soaps of higher fatty acids having 12 to 18 carbon atoms, namely those of sodium, potassium, ammonium, or amines, such as those mentioned above in reference to the salts of the acidic copolymers; alkali metal higher fatty alcohol sulfates or sulfonates having 8 to 18 carbon atoms, alkyl-substituted aryl sulfonates in which the alkyl groups contain at least a total of 8 carbon atoms, such as sodium t-octylphenylsulfonate.

The non-ionic emulsifiers or dispersing agents that may be used for preparing the monomeric emulsions before copolymerization or dispersions of the polymer after polymerization include the following: alkylphenoxy-polyethoxyethanols having alkyl groups of about seven to eighteen carbon atoms and 6 to 60 or more oxyethylene units, such as heptylphenoxy-polyethoxyethanols, octylphenoxy-polyethoxyethanols, methyl-octylphenoxy-polyethoxyethanols, nonylphenoxy-polyethoxyethanols, do-

decylphenoxy-polyethoxyethanols, and the like; polyethoxyethanol derivatives of methylene linked alkyl phenols; sulfur-containing agents such as those made by condensing 6 to 60 or more moles of ethylene oxide with nonyl, dodecyl, tetradecyl, t-dodecyl, and the like mercaptans or with alkylthiophenols having alkyl groups of six to fifteen carbon atoms; ethylene oxide derivatives of long-chained carboxylic acids, such as lauric, myristic, palmitic, oleic, and the like or mixtures of acids such as found in tall oil containing 6 to 60 oxyethylene units per molecule; analogous ethylene oxide condensates of long-chained alcohols, such as octyl, decyl, lauryl, or cetyl alcohols, ethylene oxide derivatives of etherified or esterified polyhydroxy compounds having a hydrophobic hydrocarbon chain, such as sorbitan monostearate containing 6 to 60 oxyethylene units, etc.; block copolymers of ethylene oxide and propylene oxide comprising a hydrophobic propylene oxide section combined with one or more hydrophilic ethylene oxide sections.

The process of the present invention is adapted to produce papers and other fibrous products having increased strengths. The papers and felts obtained may be used for making paper boards, paper bags of the single wall or multi wall type, backings for flooring such as linoleum, roofing felts, waterproof or moisture-vaporproof paper, paper or board containers or cartons for milk, butter, foods, etc., resin-impregnated laminating paper, abrasives composed of resin-impregnated paper coated with abrasive particles, moulded articles, premoulded articles, electrical insulators, filter paper, heat-insulating paper, or loose masses of unfelted and unmoulded impregnated cellulose stock used for air filters, dust filters, heat-insulation and the like.

The following examples are illustrative of the invention, parts being by weight unless otherwise indicated:

EXAMPLE 1

(a) A mass of bleached sulfite pulp (3.44 parts dry weight) are soaked in about 270 parts of an aqueous 33% papermaker's alum solution for 15 minutes, drained, rinsed with water for 15 seconds, quickly redispersed in 200 parts of fresh water and promptly thereafter 4.3 parts of an aqueous dispersion containing 40% by weight of an emulsion copolymerized poly(methyl acrylate), dispersed by about 0.07 part of sodium lauryl sulfate, is added and mixed in. One minute thereafter, the pulp slurry is deposited as a sheet (designated sheet A) on a screen, which is then dried and subjected to a Mullen burst test and an MIT fold test. The weight of the sheet is given in grams per 100 sq. in. of area and the test results are given in Table I following.

(b) The same weight of bleached sulfite pulp as in part (a) is dispersed in 200 parts of water and deposited as a sheet (sheet B) to provide a test control sheet containing no alum or polymer.

(c) The procedure of part (a) is repeated except the rinse is omitted. Sheet C thereby obtained is tested as before.

(d) The same weight of bleached sulfite pulp as in part (a) is dispersed in 200 parts of water, 4.3 parts of the same poly(methyl acrylate) dispersion is added and mixed in. Then 13.5 parts of an aqueous 33% papermaker's alum solution is added to provide an excess of alum over the amount equivalent to the emulsifier. After mixing one minute, a sheet (sheet D) is formed and tested as before.

Table I

Sheet	Wt., g./100 sq. in.	Mullen Burst, lbs./sq. in.	MIT Fold
A-----	6.35	82	1,346
B-----	4.79	17	5
C-----	5.60	63	734
D-----	6.15	68	883

The results in Table I show a marked improvement in sheet A obtained by the process of the present invention as compared to sheet D obtained by the usual procedure involving addition of the polymer prior to that of alum. Sheet C shows the importance of the rinsing step in the procedure of the present invention.

EXAMPLE 2

(a) 3.5 parts of bleached sulfite pulp (dry) is soaked in 270 parts of an aqueous 33% papermaker's alum solution for 15 minutes, drained, rinsed 15 seconds with water, redispersed rapidly in 200 parts of water, and promptly thereafter about 4.37 parts of an aqueous dispersion containing about 40% by weight of an emulsion polymerized poly(methyl acrylate) dispersed by about 0.07 part of sodium lauryl sulfate is added. One minute thereafter, the slurry is sheeted, and the sheet (sheet E) is dried and tested for tensile strength, Mullen burst, edge tear, and MIT fold. See Table II.

(b) 3.5 parts of the same bleached sulfite pulp are soaked in 200 parts of water for 15 minutes and then dispersed in the water. Then 4.37 parts of an aqueous dispersion containing about 40% by weight of an emulsion polymerized poly(methyl acrylate) dispersed by about 0.07 part of sodium lauryl sulfate is added. After intimate mixture, 13.5 parts of an aqueous 33% papermaker's alum solution is added and mixed in. After one minute, the slurry is formed into sheet F, dried and tested. See table II.

Table II

Sheet	Wt., g./100 sq. in.	Mullen Burst, lbs./sq. in.	Tensile, lbs./in.	Edge Tear, lbs./in.	MIT Fold
E-----	6.20	82	33	16.8	2,006
F-----	5.55	67	28	15.6	794

Table II shows marked improvement in sheets when made by the procedure of the present invention.

EXAMPLE 3

The procedure of Example 2(a) is repeated substituting 9 parts of an aqueous dispersion containing about 40% of an emulsion polymerized copolymer of 60% acrylonitrile, 30% ethyl acrylate, and 10% butyl methacrylate using a non-ionic emulsifier consisting essentially of t-octylphenoxypolyethoxyethanol containing about 10 oxyethylene units. Excellent and uniform disposition of polymer on the fibers in the sheet is obtained.

EXAMPLE 4

The procedure of Example 2(a) is repeated with similar results when unbleached kraft is substituted for the pulp therein.

EXAMPLE 5

The procedure of Example 2(a) is repeated replacing the alum solution with a corresponding volume of a 15% potassium alum solution. Excellent deposition and distribution of the polymer on the fibers of the sheet are obtained.

EXAMPLE 6

The procedure of Example 2(a) is repeated replacing the polymer dispersion with a dispersion containing the same weight of a copolymer of about 65% ethyl acrylate, about 33% of methyl methacrylate and about 2% of methacrylic acid dispersed by the same non-ionic agent as described in Example 1(a). Similar results are obtained.

EXAMPLE 7

The procedure of Example (a) is repeated replacing the polymer dispersion with a dispersion containing the same weight of a copolymer of about 65% ethyl acrylate, about 33% of methyl methacrylate and about 2% of methacrylic acid dispersed by a mixture of 0.03 part of

the same non-ionic agent as described in Example 1(a) and 0.04 part of sodium lauryl sulfate. Similar results are obtained.

It is to be understood that changes and variations may be made without departing from the spirit and scope of the invention as defined by the appended claims.

I claim:

1. A process for making fibrous sheets which comprises treating cellulose fibers in an aqueous solution containing an aluminum salt dissolved therein, the resultant mixture of fibers and salt solution containing at least 10% by weight of the aluminum salt, removing excess solution from the fibers, rapidly rinsing the fibers with water, rapidly redispersing the rinsed fibers in water to form a suspension thereof having a consistency of 0.1 to 6% by weight of fibers on the weight of water, and then, promptly after redispersing the fibers, mixing into the fiber suspension an aqueous dispersion of a water-insoluble addition polymer, in an amount from 1 to 150% by weight of the polymer based on the weight of the fibers, to thereby deposit the polymer on the fibers, and then forming a sheet from the resulting fiber suspension, the steps of the process prior to the aforesaid mixing step serving to provide aluminum ions and anions of said salt on the fibers when the polymer is mixed into the fiber suspension.

2. A process for making fibrous sheets which comprises treating cellulose fibers in an aqueous solution containing an aluminum salt dissolved therein, the resultant mixture of fibers and salt solution containing at least 10% by weight of the aluminum salt, removing excess solution from the fibers, rapidly rinsing the fibers with water, rapidly redispersing the rinsed fibers in water to form a suspension thereof having a consistency of 0.1 to 6% by weight of fibers based on the weight of water, and then, promptly after redispersing the fibers, mixing into the fiber suspension an aqueous dispersion of a water-insoluble addition polymer, in an amount from 25 to 150% by weight of the polymer based on the weight of the fibers, to thereby deposit the polymer on the fibers, and then forming a sheet from the resulting fiber suspension, the steps of the process prior to the aforesaid mixing step serving to provide aluminum ions and anions of said salt on the fibers when the polymer is mixed into the fiber suspension.

3. A process for making fibrous sheets which comprises treating cellulose fibers in an aqueous solution containing an aluminum salt dissolved therein, the resultant mixture of fibers and salt solution containing at least 10% by weight of the aluminum salt, removing excess solution from the fibers, rapidly rinsing the fibers with water, rapidly redispersing the rinsed fibers in water to form a suspension thereof having a consistency of 0.1 to 6% by weight of fibers based on the weight of water, and then, promptly after redispersing the fibers, mixing into the fiber suspension an aqueous dispersion of a water-insoluble addition polymer dispersed by a non-ionic dispersing agent to thereby deposit the polymer on the fibers, the amount of polymer being from 1 to 150% by weight, based on the weight of the fibers, and then forming a sheet from the resulting fiber suspension, the steps of the process prior to the aforesaid mixing step serving to provide aluminum ions and anions of said salt on the fibers when the polymer is mixed into the fiber suspension.

4. A process for making fibrous sheets which comprises treating cellulose fibers in an aqueous solution containing an aluminum salt dissolved therein, the resultant mixture of fibers and salt solution containing at least 10% by weight of the aluminum salt, removing excess solution from the fibers, rapidly rinsing the fibers with water, rapidly redispersing the rinsed fibers in water to form a suspension thereof having a consistency of 0.1 to 6% by weight of fibers based on the weight of water, and then, promptly after redispersing the fibers, mixing into the fiber suspension an aqueous dispersion of a water-insoluble addition polymer dispersed by an anionic dispersing

agent to thereby deposit the polymer on the fibers, the amount of polymer being from 1 to 150% by weight, based on the weight of the fibers, and then forming a sheet from the resulting fiber suspension, the steps of the process prior to the aforesaid mixing step serving to provide aluminum ions and anions of said salt on the fibers when the polymer is mixed into the fiber suspension.

5. A process for making fibrous sheets which comprises treating cellulose fibers in an aqueous solution containing an aluminum salt dissolved therein, the resultant mixture of fibers and salt solution containing at least 10% by weight of the aluminum salt, removing excess solution from the fibers, rapidly rinsing the fibers with water, rapidly redispersing the rinsed fibers in water to form a suspension thereof having a consistency of 0.1 to 6% by weight of fibers based on the weight of water, and then, promptly after redispersing the fibers, mixing into the fiber suspension an aqueous dispersion of a water-insoluble addition polymer dispersed by a mixture of a non-ionic and an anionic dispersing agent to thereby deposit the polymer on the fibers, the amount of polymer being from 1 to 150% by weight, based on the weight of the fibers, and then forming a sheet from the resulting fiber suspension, the steps of the process prior to the aforesaid mixing step serving to provide aluminum ions and anions of said salt on the fibers when the polymer is mixed into the fiber suspension.

6. A process for making fibrous sheets which comprises treating cellulose fibers in an aqueous solution containing an aluminum salt dissolved therein, the resultant mixture of fibers and salt solution containing at least 10% by weight of the aluminum salt, removing excess solution from the fibers, rapidly rinsing the fibers with water, rapidly redispersing the rinsed fibers in water to form a suspension thereof having a consistency of 0.1 to 6% by weight of fibers based on the weight of water, and then, promptly after redispersing the fibers, mixing into the fiber suspension an aqueous dispersion of a water-insoluble addition polymer containing monomeric units selected from the group consisting of carboxylic acids, am-

monium and alkali metal salts thereof and salts thereof with water-soluble amines to thereby deposit the polymer on the fibers, said polymer being dispersed in the dispersion by a non-ionic dispersing agent, the amount of polymer mixed in being from 1 to 150% by weight, based on the weight of the fibers, and then forming a sheet from the resulting fiber suspension, the steps of the process prior to the aforesaid mixing step serving to provide aluminum ions and anions of said salt on the fibers when the polymer is mixed into the fiber suspension.

7. A process for making fibrous sheets which comprises treating cellulose fibers in an aqueous solution containing an aluminum salt dissolved therein, the resultant mixture of fibers and salt solution containing at least 10% by weight of the aluminum salt, removing excess solution from the fibers, rapidly rinsing the fibers with water, rapidly redispersing the rinsed fibers in water to form a suspension thereof having a consistency of 0.1 to 6% by weight of fibers based on the weight of water, and then, promptly after redispersing the fibers, mixing into the fiber suspension an aqueous dispersion of a water-insoluble addition polymer containing monomeric units selected from the group consisting of carboxylic acids, ammonium and alkali metal salts thereof and salts thereof with water-soluble amines to thereby deposit the polymer on the fibers, said polymer being dispersed in the dispersion by a mixture of a non-ionic and an anionic dispersing agent, the amount of polymer mixed in being from 1 to 150% by weight, based on the weight of the fibers, and the steps of the process prior to the aforesaid mixing step serving to provide aluminum ions and anions of said salt on the fibers when the polymer is mixed into the fiber suspension.

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