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3,049,469

APPLICATION OF COATING OR IMPREGNATING MATERIALS TO FIBROUS MATERIAL

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The present invention relates to the application of certain water-soluble, carboxyl-containing materials to fibrous cellulosic material such as paper stock followed, if desired, by forming the resulting pretreated cellulosic material into fibrous felted sheets or articles such as paper, paper board, molded or premolded cellulosic articles and the like.

Heretofore, the principal methods of incorporating water-soluble, carboxyl-containing materials into a sheet of pulp or paper have been by impregnation of the formed sheet by an aqueous solution of the material to be incorporated or by addition of the material to an aqueous suspension or slurry of pulp. Thus, it is common practice to add such materials to the pulp slurry in the beater, stock chest or at any other point in the papermaking system prior to sheet formation, preceded or followed by the addition of alum. By this procedure, the materials are precipitated and the resulting flocs are entangled or mixed with the fibrous paper stock and carried into the finished paper.

While this procedure works out quite well in some cases, it is subject to disadvantages in others. Thus, in the preparation of paper products where an acidic papermaking system is undesirable or where aluminum and similar polyvalent cations must be kept out of the system, the use of alum is disadvantageous and, in most cases, unsatisfactory.

A principal object of the present invention is the provision of an improved process for the incorporation of certain water-soluble, carboxyl-containing materials into fibrous cellulosic material in a manner such that the above difficulties and/or disadvantages are avoided.

Another object of the invention is the provision of an improved process for the manufacture of fibrous materials wherein certain water-soluble, carboxyl-containing materials are effectively and uniformly distributed on, and firmly anchored to, the fibrous material.

A more specific object of the invention is the provision of novel fibrous products such as paper, paperboard and the like having improved wet and dry strengths as well as other desirable properties.

In accordance with the present invention, the above and other objects are attained by the action of certain water-soluble cationic thermosetting polyamide-epichlorohydrin resins in an aqueous system containing fibrous cellulosic material of the type of paper pulp suspended therein together with certain water-soluble, carboxyl-containing compounds. It has been found that in this system the cationic resin not only flocculates the water-soluble, carboxyl-containing compound but serves to anchor it to the fibers by the formation of a direct bond between the cationic resin and the water-soluble carboxyl-containing compound and by the affinity of the cationic resin for the fiber.

In carrying out the process of the invention, as applied, for example, in the art of papermaking, the cationic resin and the water-soluble, carboxyl-containing material, each preferably in dilute aqueous solution, are added to a dilute

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aqueous suspension of paper pulp as in the beater of a papermaking system, following which the pulp is sheeted and dried in the usual manner. The paper product formed when the water-soluble, carboxyl-containing material, for example, is an acrylic dry strength additive has improved dry and wet strengths. Moreover, the improvement in wet strength is greater than would be expected from the combined action of the ingredients thus indicating a synergistic effect when the two are used together.

The order of addition of the water-soluble, carboxyl-containing compound and the cationic resin is important for the attainment of optimum results, i.e., maximum increase in dry and wet strengths. Thus, while some improvements in dry and wet strengths are obtained when the cationic resin is added with or after the water-soluble, carboxyl-containing compound, substantially greater improvements are obtained when the cationic resin is added to the pulp fiber slurry first and thoroughly blended into the system prior to the addition of the water-soluble, carboxyl-containing compound. The papermaking system (pulp slurry and dilution water) may be acidic, neutral or alkaline. The preferred pH range is from about 5 to 9. The cationic resin and the water-soluble, carboxyl-containing compound are desirably added to the system in the form of dilute aqueous solutions at solids concentrations from about 1 to 10%.

The amount of water-soluble, carboxyl-containing material to be added will depend on a number of factors such as the particular material used, the results desired and so on. In the case of dry-strength additives such as acrylic polymers and copolymers, amounts from about 0.25% to about 3%, based on the weight of dry fiber, may be used with quite satisfactory results. While more than 3% of these materials, such as up to 10% or more may be used, this will usually not be necessary. In the case of other water-soluble, carboxyl-containing compounds, somewhat larger amounts may be required to produce a desired result. In general, however, it may be stated that from about 0.25% to about 10% of such material will be adequate in most cases.

The amount of cationic resin to be added will likewise vary with many factors such as the particular resin used, the results desired and so on. In most cases from about 0.1% to about 2% of the resin, based on the dry weight of fiber, will give satisfactory results. However, larger amounts, say, up to about 5% may be used to obtain special effects such as unusually high wet strength and so on.

The cationic thermosetting polyamide-epichlorohydrin resins contemplated for use herein comprise a water-soluble polymeric reaction product of epichlorohydrin and a polyamide derived from a polyalkylene polyamine and a C₃-C₁₀ saturated aliphatic dicarboxylic acid. It has been found that resins of this type are uniquely effective for effecting flocculation, deposition and anchoring of water-soluble, carboxyl-containing compounds to fibers in aqueous suspension.

In the preparation of these cationic thermosetting resins, the dicarboxylic acid is first reacted with the polyalkylene polyamine under conditions such as to produce a water-soluble polyamide containing the recurring groups



where n and x are each 2 or more and R is the divalent hydrocarbon radical of the dicarboxylic acid. This water-

soluble polyamide is then reacted with epichlorohydrin to form the water-soluble cationic thermosetting resin.

The dicarboxylic acids contemplated for use in preparing these resins are the C_3 - C_{10} saturated aliphatic dicarboxylic acids such as succinic, glutaric, adipic and the like. The saturated dicarboxylic acids having from 4 to 8 carbon atoms in the molecule are preferred. Blends of two or more of the saturated dicarboxylic carboxylic acids may also be used.

A variety of polyalkylene polyamines including polyethylene polyamines, polypropylene polyamines, polybutylene polyamines and so on may be employed of which the polyethylene polyamines represent an economically preferred class. More specifically, the polyalkylene polyamines contemplated for use may be represented as polyamines in which the nitrogen atoms are linked together by groups of the formula $-C_nH_{2n}-$ where n is a small integer greater than unity and the number of such groups in the molecule ranges from two up to about eight. The nitrogen atoms may be attached to adjacent carbon atoms in the group $-C_nH_{2n}-$ or to carbon atoms further apart, but not to the same carbon atom. This invention contemplates not only the use of such polyamines as diethylenetriamine, triethylenetetramine, tetraethylenepentamine, dipropylenetriamine and the like, which can be obtained in reasonably pure form, but also mixtures and various crude polyamine materials. For example, the mixture of polyethylene polyamines obtained by the reaction of ammonia and ethylene dichloride, refined only to the extent of removal of chlorides, water, excess ammonia and ethylenediamine, is a very satisfactory starting material. The term "polyalkylene polyamine" employed in the claims, therefore, refers to and includes any of the polyalkylene polyamines referred to above or to a mixture of such polyalkylene polyamines.

It is desirable, in some cases, to increase the spacing of secondary amino groups on the polyamide molecule in order to change the reactivity of the polyamide-epichlorohydrin complex. This can be accomplished by substituting a diamine such as ethylenediamine, propylenediamine, hexamethylenediamine and the like for a portion of the polyalkylene polyamine. For this purpose, up to about 80% of the polyalkylene polyamine may be replaced by a molecularly equivalent amount of the diamine. Usually, a replacement of about 50% or less will serve the purpose.

The temperatures employed for carrying out the reaction between the dicarboxylic acid and the polyalkylene polyamine may vary from about 110° C. to about 250° C. or higher at atmospheric pressure. For most purposes, however, temperatures between about 160° C. and 210° C. have been found satisfactory and are preferred. Where reduced pressures are employed, somewhat lower temperatures may be utilized. The time of reaction depends on the temperatures and pressures utilized and will ordinarily vary from about ½ to 2 hours, although shorter or longer reaction times may be utilized depending on reaction conditions. In any event, the reaction is desirably continued to substantial completion for best results.

In carrying out the reaction, it is preferred to use an amount of dicarboxylic acid sufficient to react substantially completely with the primary amine groups of the polyalkylene polyamine but insufficient to react with the secondary amine groups to any substantial extent. This will usually require a mole ratio of polyalkylene polyamine to dicarboxylic acid of from about 0.9:1 to about 1.2:1. However, mole ratios of from about 0.8:1 to about 1.4:1 may be used with quite satisfactory results. Mole ratios outside of these ranges are generally unsatisfactory. Thus, mole ratios below about 0.8:1 result in a gelled product or one having a pronounced tendency to gel while mole ratios above 1.4:1 result in low molecular weight polyamides. Such products when reacted with epi-

chlorohydrin, do not produce resins having the desired efficiency for use herein.

In converting the polyamide, formed as above described, to a cationic thermosetting resin, it is reacted with epichlorohydrin at a temperature from about 45° C. to about 100° C. and preferably between about 45° C. and 70° C. until the viscosity of a 20% solids solution at 25° C. has reached about C or higher on the Gardner-Holdt scale. This reaction is preferably carried out in aqueous solution to moderate the reaction. pH adjustment is usually not necessary. However, since the pH decreases during the polymerization phase of the reaction it may be desirable, in some cases, to add alkali to combine with at least some of the acid formed.

When the desired viscosity is reached, sufficient water is then added to adjust the solids content of the resin solution to the desired amount, i.e., about 10% more or less, the product cooled to about 25° C. and then stabilized by adding sufficient acid to reduce the pH at least to about 6 and preferably to about 5. Any suitable acid such as hydrochloric, sulfuric, nitric, formic, phosphoric and acetic acid may be used to stabilize the product. However, hydrochloric acid is preferred.

In the polyamide-epichlorohydrin reaction, it is preferred to use sufficient epichlorohydrin to convert all secondary amine groups to tertiary amine groups. However, more or less may be added to moderate or increase reaction rates. In general, satisfactory results may be obtained utilizing from about 0.5 mole to about 1.8 moles of epichlorohydrin for each secondary amine group of the polyamide. It is preferred to utilize from about 1.0 mole to about 1.5 moles for each secondary amine group of the polyamide.

The carboxyl-containing compounds contemplated for use herein are the water-soluble or water-dispersible polymers and copolymers of acrylic acid and methacrylic acid such as acrylamide-acrylic acid, methacrylamide-acrylic acid, acrylonitrile-acrylic acid, methacrylonitrile-acrylic acid; copolymers involving one of several alkyl acrylates and acrylic acid, copolymers involving one of several alkyl methacrylates and acrylic acid, copolymers involving one of several alkyl vinyl ethers and acrylic acid; and similar copolymers in which methacrylic acid is substituted in place of acrylic acid in the above examples.

Exemplary of the acrylic type polymers and copolymers which may be utilized herein are those described in U.S. Patent 2,661,309 to Julian L. Azorlosa and Canadian application Serial No. 597,013, Julian L. Azorlosa, filed February 1, 1950, now Patent No. 547,577.

The water-soluble or water-dispersible compounds which may be utilized herein also include condensates of lower alkylene oxides with polymers of acrylic acid, methacrylic acid and itaconic acid having average molecular weights above about 1000 and condensates of lower alkylene oxides with copolymers of acrylic acid, methacrylic acid and itaconic acid containing at least about 35 mole percent, and preferably at least about 50 mole percent, of one or more of these acids as the substituent monomer units. Polymerizable compounds which may be copolymerized with one or more of these acids or with salts of such acids include esters of acrylic acid, methacrylic acid, itaconic acid, maleic acid, fumaric acid and citraconic acid and monohydric alcohols such as methyl, butyl, octyl, dodecyl, cyclohexyl and so on; vinyl and vinyloxy-alkyl esters of carboxylic acids such as acetic, propionic and the like; vinyl ethers such as ethyl vinyl ether and butyl vinyl ether; acrylamide; methacrylamide; and so on. Preparation of these carboxyl-containing polymers and copolymers and the condensation of same with alkylene oxides may be carried out by well-known procedures. In the latter reaction, the proportion of alkylene oxide, introduced may vary from 1 mol percent to 250 mole percent, and preferably from about 10 mole percent to about 95 mole percent of the carboxyl-containing units of the polymer.

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The following example will illustrate the invention.

EXAMPLE

Weyerhaeuser bleached sulfite softwood pulp was beaten in pH 7 water with a Noble and Wood cycle beater to a Schopper-Riegler freeness of 825 ml. The pulp slurry was diluted to 2.5% consistency with pH 7 water. The following chemicals were added to 2-liter portions of this slurry with stirring.

(1a) A sufficient volume of 10% aluminum sulfate solution to reduce the slurry pH to 4.5.

(1b) 1% (based on dry weight of pulp) of a dry-strength additive consisting of a 90:10 acrylamide-acrylic acid copolymer, added as a 1% aqueous solution. After a few minutes of stirring, sufficient alum solution was added to reduce the slurry pH to 4.5 as in (1a) above. This acrylamide-acrylic acid copolymer was prepared by adding the following materials, in the order listed, to a pressure-resistant polymerization bottle:

Recrystallized acrylamide -----g--	9.0
Distilled water -----g--	185.0
Distilled acrylic acid -----g--	1.0
Isopropanol -----g--	0.5
1% solution of $K_2S_2O_8$ in distilled water ----cc--	5.0

Immediately after addition of the catalyst, the contents of the bottle were blanketed with nitrogen for several minutes. The bottle was then capped and evacuated with a water aspirator for one minute. Nitrogen was added to a total pressure of 45 p.s.i., and the bottle was re-evacuated. This flushing and evacuation process was repeated once more, after which nitrogen was added to a total pressure of 30 p.s.i. The polymerization bottle was then placed on a tumbler at 22° C. and rotated for several days. The viscous solution which resulted was shortstopped with hydroquinone, and a total solids determination showed that complete conversion to a polymeric product had been obtained. The solution was diluted to a concentration of 1% by weight (specific viscosity=150), and its pH was adjusted to 8.2 with NaOH. It was then stored at 1° C. until use.

(1c) 1% (based on dry weight of pulp) of a polyamide-epichlorohydrin condensation product as an aqueous solution. This condensation product was prepared by the following procedure: To a mixture of 1914 g. of triethylenetetramine and 600 g. of water, 1740 g. of adipic acid was added in several portions, allowing one portion to dissolve before the next was added. The resulting mixture was heated to 195–200° C. for 1½ hours, and water was distilled off continuously during the entire heating period. The mixture was then cooled to 140° C. under vacuum and 3 liters of 80° C. water was then added cautiously. The polyamide product had a total solids content of 54.4% and an acid number of 3.6. Water was used to dilute 2162 g. of this product to a total weight of 10,751 g. The aqueous solution was stirred and heated to 45° C. At this stage, the addition of 1025 g. of epichlorohydrin was started. The addition was complete by the time the temperature reached 60° C. The mixture was then held between 60° and 70° C. until its Gardner-Holdt viscosity reached a value of E. Then 9 liters of water and 250 ml. of 3.7% HCl solution were added. The final product had a pH of 5.75 and a total solids content of 11.0%.

(1d) 1% of the polyamide-epichlorohydrin condensation product described in (1c) above (based on dry weight of pulp). After a few minutes of stirring, an equal weight of the acrylamide-acrylic acid copolymer described in (1b) above was added to the slurry. The final slurry pH value for both (1c) and (1d) was about 7.0.

All slurry samples were diluted to 0.25% consistency with pH 7 water and then diluted further to a deckle box consistency of 0.025% in order to form 40-pound basis weight (24 x 36–500 sheet ream) handsheets, using a Noble and Wood sheetmaking apparatus. A closed white

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water system was employed. Formed sheets were wet pressed to 35–45% solids content and then dried at 250° F. on a steam drum drier. After conditioning for several days at 73° F. and 50% relative humidity, the sheets were tested in the same environment for various paper strength properties, using standard testing equipment. Strength data were corrected to 40 pounds/ream basis weight by use of the linear relation $S=KB$, where S represents the strength property and B represents sheet basis weight. The results are set forth in the table below.

Table

Experiment	Dry Strength Properties (Corrected to 40 lb./R. basis wt.)		Percent Increase in Tear-Burst Sheet Strength of Control ¹	Uncured Wet Tensile Strength (after 2-hour soak in distilled water), lb./in.
	Elmendorf Tear (g./sheet)	Mullen Burst (p.s.i.)		
1a-----	86	20	Control	not tested
1b-----	60	35	16.4	1.6
1c-----	74	25	4.5	3.4
1d-----	54	39	20.0	6.8

¹ TAPPI 40, p. 499, July 1957.

These data show that when the polyamide-epichlorohydrin resin is used with the acrylic copolymer dry strength additive, there is an improvement in overall tear-burst sheet strength of 20%, as compared with the alumed control, whereas the resin alone produced an improvement of 4.5% and the alum plus dry strength additive produced an improvement of 16.4%. Moreover, not only does the polyamide-epichlorohydrin resin produce wet strength, while the alum treatment does not, but the combination of the acrylic copolymer with the resin shows a synergistic effect which almost doubles the wet tensile strength produced by the resin alone. Thus, the dry strength additive and the resin mutually enhance the separate effects of each.

The present invention provides a number of advantages. Thus, the use of the polyamide-epichlorohydrin resins herein described permit the effective incorporation of the described water-soluble, carboxyl-containing polymers into fibrous cellulosic materials without the use of alum, thus avoiding the necessities of an acidic papermaking system and the presence of polyvalent cations which might have other undesirable effects. Moreover, the use of these resins in conjunction with a water-soluble carboxyl-containing compound, such as an acrylic dry-strength additive, results in an unexpected improvement in wet strength. And, finally, by virtue of the reduced content of polyamine in these polyamide-epichlorohydrin resins, as compared, for example, with polyamine-epichlorohydrin resins, these advantages and improvements may be attained with greater economies in operation and with unexpected improvements in certain properties, such as wet strength, not obtainable with the latter type of resin.

The term "water-soluble," as used herein, is intended to refer to materials which are dispersible in water without the aid of a dispersing agent as well as those which are truly soluble in water.

While specific embodiments of the invention have been illustrated and described herein, it will be understood that changes and variations may be made without departing from the scope of the invention as defined in the claims which follow.

What I claim and desire to protect by Letters Patent is:

1. A process for impregnating fibrous cellulosic material with a water-soluble, carboxyl-containing material selected from the group consisting of polymers of acrylic acid, copolymers of acrylic acid and compounds copolymerizable therewith selected from the group consisting of acrylamide, methacrylamide, acrylonitrile and methacrylonitrile, polymers of methacrylic acid, and copolymers of methacrylic acid and compounds copolymerizable there-

with selected from the group consisting of acrylamide, methacrylamide, acrylonitrile and methacrylonitrile, which comprises forming an aqueous suspension of the fibrous cellulosic material at a consistency from about 0.1% to about 5%, adding to such aqueous suspension (1) from about 0.1% to about 5%, based on the dry weight of fibrous cellulosic material, of a cationic thermosetting resin obtained by reacting a polyalkylene polyamine having two primary amine groups and at least one secondary amine group with a C₃-C₁₀ saturated aliphatic dicarboxylic acid at a temperature from about 110° C. to about 250° C. and in a mole ratio of polyalkylene polyamine to dicarboxylic acid of from about 0.8:1.0 to about 1.4:1.0 to form a long-chain polyamide having secondary amine groups, and then reacting the polyamide with epichlorohydrin at a temperature from about 45° C. to about 100° C. and in a mole ratio of epichlorohydrin to secondary amine groups of said polyamide from about 0.5:1 to about 1.8:1, and (2) a water-soluble, carboxyl-containing mate-

rial selected from the indicated group, whereby a substantial portion of said water-soluble, carboxyl-containing material is deposited on and attached to said fibrous material together with said cationic thermosetting resin.

2. A process in accordance with claim 1 wherein the water-soluble, carboxyl-containing compound is a copolymer of acrylic acid and acrylamide.

References Cited in the file of this patent

UNITED STATES PATENTS

2,601,597 Daniel June 24, 1952

FOREIGN PATENTS

711,404 Great Britain June 30, 1954

OTHER REFERENCES

Ser. No. 323,512, Hagedorn (A.P.C.), published Apr. 20, 1943.