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3,269,852

**CELLULOSIC PRODUCT OF IMPROVED
STRENGTH AND PROCESS THEREFOR**

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This invention relates to the improvement of the physical properties of cellulosic materials. In one of its more particular aspects this invention relates to a process for producing cellulosic materials of greatly enhanced strength characteristics, particularly high wet strength.

It has been known for some time that cellulosic fibers dispersed in water have a negative surface potential and are therefore not substantive to various negatively charged materials which could otherwise be used to impart desired properties to the cellulosic fibers. For example, the polymeric aldehydes produced by the periodate oxidation of polysaccharides, referred to hereinafter as dialdehyde polysaccharides, are known to contribute strength characteristics to cellulosic fibers when utilized as additives to the wet end of the paper making process. However, the addition of dialdehyde polysaccharides to the negatively charged cellulosic fibers has posed certain problems which it has been possible to solve only by resorting to involved and time consuming operations in which the cellulosic fibers have been pretreated with chemical agents which reverse the charge of the cellulosic surface prior to the addition of a dialdehyde polysaccharide to the cellulosic fibers.

For instance, the aqueous fiber slurries have been contacted with such strongly cationic water-soluble materials as large amounts of alum, aqueous dispersions of cationic starches, polymeric amides and other suitable cationic substances. This procedure is sometimes referred to as fiber pretreatment and the materials used for this purpose are known as retention aids or coupling agents. Once the cellulosic fibers have been so treated, strongly anionic dispersions of dialdehyde polysaccharides may be added to the pretreated fibers and retained by means of electrostatic attraction. In recent years a variety of procedures have been developed in which dialdehyde starch, a preferred dialdehyde polysaccharide, has been utilized as a wet end additive. Such procedures are described in G. E. Hamerstrand, B. T. Hofreiter, C. L. Mehlretter, W. E. Schache and D. J. Kay, Tappi, 44, 430 (1961), and in B. T. Hofreiter, G. E. Hamerstrand, D. J. Kay and C. E. Rist, Tappi, 45, 177 (1962).

Most such processes utilize a dispersion of a dialdehyde polysaccharide in the presence of an inorganic bisulfite salt to render the dialdehyde polysaccharide strongly anionic.

Thus, in the prior art processes it is necessary to (1) add a suitable retention aid or coupling agent to the cellulosic fibers and (2) thereafter add to the pretreated cellulosic fibers a dispersion of a strongly anionic dialdehyde polysaccharide dispersion. In practice the process is carried out at various points in the manufacture of cellulosic web materials. For instance, addition has been suggested at the beater, the headbox, the fan pump, and various other points at the wet end of the manufacturing process.

Certain decided disadvantages to the aforementioned methods for the treatment of cellulosic fibers have been encountered. One of these disadvantages is the uneconomical requirement for the use of relatively large amounts of retention aid or coupling agent. It is believed that the use of substantial proportions of such cationic materials results in surface areas of the fibers

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which would otherwise be available as potential reaction sites for interaction between the cellulose and the aldehyde groups of the dialdehyde polysaccharide being occupied by these materials. This may be visualized as a situation wherein the strength-imparting material has fewer contact points available at the fibers' surfaces than are needed for full strength development.

Another disadvantage to the use of the aforementioned methods for imparting high wet strength to paper and other cellulosic materials lies in the problems inherent in the use of an inorganic bisulfite salt. It has been found that the use of bisulfite salts in the preparation of dialdehyde polysaccharide dispersions limits the concentration of these dispersions to a maximum of about 3%. The reason for this is that at higher concentrations highly viscous thixotropic gels are formed during the cooking procedures. These gels have considerable resistance to break-down into fragments of lower molecular weight which break-down is necessary for their successful use. Furthermore, no consistent heat transfer is possible after reaching the peak gel stage.

It is, accordingly, a principal object of this invention to provide cellulosic materials which are characterized by having excellent strength characteristics, particularly with respect to wet strength.

Another object of this invention is to provide a process for improving the properties of cellulosic fibers which is more economical and more effective than the aforementioned prior art processes.

A further object of this invention is to provide such a process which is characterized by practical convenience coupled with the attainment of optimum results.

Yet another object of this invention is to provide a process for the preparation of cellulosic web materials which process may be readily adapted to conventional techniques utilized in the manufacture of such materials. Other objects and advantages of this invention will be apparent to those skilled in the art from the following detailed disclosure and description.

It has now been found that the disadvantages inherent in previously available processes for the provision of cellulosic materials having improved strength characteristics can be overcome by means of a simple and convenient technique for the treatment of cellulosic fibers. The process generally comprises the cationization of a dialdehyde polysaccharide with a suitably formulated cationizing agent under conditions such that interaction between the cationizing agent and the dialdehyde polysaccharide results in the provision of a product which is cationic in nature and definitely substantive to anionic cellulose. The cationic nature of the reaction product between the dialdehyde polysaccharide and the cationizing agent can be demonstrated by means of electrophoresis. As developer certain anionic dyes such as Halopont Blue RNM (Du Pont) can be used. This process results in full availability of the cellulosic fibers to adherence by a cationized dialdehyde polysaccharide. Other advantages, yet, will accrue from the operation of this process. These additional advantages will be further disclosed below.

For the operation of the process of this invention a dialdehyde polysaccharide is first dispersed in water to form an aqueous dispersion of the dialdehyde polysaccharide. Dispersion is accomplished by heating a dialdehyde polysaccharide in water to a temperature of about from 60° C. to 90° C. The concentration of the dialdehyde polysaccharide in the aqueous dispersion may be about from 1% to 30% by weight, preferably about from 3% to 10%. Cooking the dialdehyde polysaccharide in water functions to rupture the granules of the dialdehyde polysaccharide. The cook is generally considered to be complete when no unruptured granules are found to be

present. This can be ascertained by means of centrifugation or by other appropriate analytical means. Sometimes the dispersion of the dialdehyde polysaccharide can be facilitated by the use of a small amount of a buffer salt such as sodium acetate, sodium citrate, monosodium phosphate, borax or sodium hexametaphosphate. The use of such salts is particularly desirable where dispersions of relatively high concentrations, for example, of above about 10% are required. In general, the amount of salt used should be in the range of about from 0.1% to 5%, preferably about from 0.5% to 2.5%, of the weight of dialdehyde polysaccharide used. Both the temperature of dispersion and the necessity for use of a salt are to a large extent dependent upon the composition of the water used for preparing the dispersion. For instance, water having a relatively high alkalinity, for example, 200 p.p.m. or higher, requires a cooking temperature, for a 3% to 5% dispersion, in the range of about from 60° C. to 70° C. Water of lower alkalinity, for example, about 100 p.p.m. or below, may require a cooking temperature of upwards of about 80° C., for instance, temperatures in the range of about from 80° C. to 90° C. It should be noted that the use of low temperatures is possible where water of high alkalinity is used or where basic reacting buffer salts are added. The total alkalinity may be defined as ten times the number of milliliters of 0.02 N sulfuric acid required to reduce the pH of a 100 milliliter water sample to pH 4.0. This test is recorded as Tappi Standard T 620 m-55, Sheet 4.

Following the step of dispersing the dialdehyde polysaccharide in water the pH of the resulting dispersion is lowered to one in the range of about from pH 3.0 to pH 4.0 and preferably about pH 3.5. The lowering of the pH of the dialdehyde polysaccharide dispersion may be conveniently accomplished by adding any dilute acid such as hydrochloric acid, sulfuric acid or formic acid. Sulfuric acid is generally preferred for this purpose. This pH adjustment prevents alkaline material which may be present in the water used for preparing the dispersion from further degrading the dialdehyde polysaccharide. Such degradation results in undesirably low wet strength being attained from use of such dispersions, especially where the dispersions are subjected to long periods of heating. This pH adjustment also exerts beneficial effects in the later processing steps serving to both catalyze the reaction between the dialdehyde polysaccharide and the cationizing agent and to prevent agglomeration upon interaction between these materials.

Following adjustment of the pH of the aqueous dialdehyde polysaccharide dispersion the cationizing agent to be used is added to the dialdehyde polysaccharide dispersion at the cooking temperature thereof. The cationizing agent is then allowed to react with the dialdehyde polysaccharide in dispersion for a period, generally, of about from one minute to 10 minutes in length. The resulting dispersion of cationized dialdehyde polysaccharide is of colloidal nature and may then be utilized in application to cellulosic fibers such as by adding said cationized dialdehyde polysaccharide to an aqueous suspension of cellulosic fibers such as found in the beater of a paper machine during the process of paper manufacture. Likewise, the addition may be at various other points in the paper making process or corresponding points in the processing of other cellulosic fibers. Wet strength increases in the range of about 100 to 1000% over the blank have been realized using this process, depending on the type of fiber and the amount of cationized dialdehyde polysaccharide added.

The suggested pH range of pH 3.0 to 4.0, and preferably pH 3.5, is an optimum one for facilitating the interaction between the dispersed dialdehyde polysaccharide and the cationizing agent. Further, the cationized dialdehyde polysaccharide formed at this pH is a hydrophilic colloid which has shown excellent stability upon prolonged storage with no formation of agglomerates. The use of

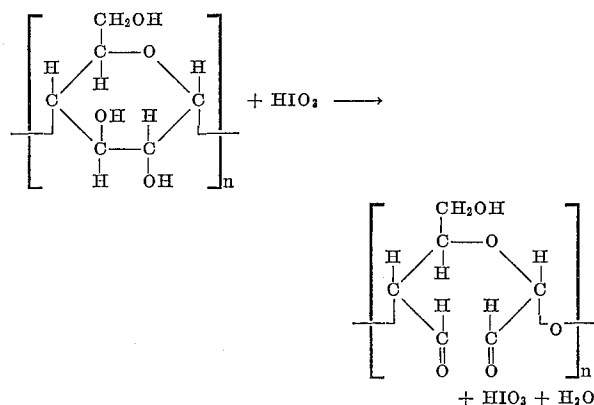
dispersions of dialdehyde polysaccharides which have not been pH adjusted as taught herein and having a pH above about pH 4.0, on the other hand, has resulted in the instantaneous agglomeration of colloidal particles upon addition of the cationizing agent. The use of such dispersions results in very little, if any, wet strength improvement.

The amount of cationizing agent added to the dispersion of the dialdehyde polysaccharide depends upon its chemical nature. Economic considerations are also involved. Optimum results vary with each type used. The general range, however, is about from 1% to 50% by weight of the dialdehyde polysaccharide, and preferably about from 10% to 30%.

As pointed out above, the cationized dialdehyde polysaccharide dispersion may be incorporated into various points in cellulose processing. For example, in the paper making process it may be incorporated into the pulp slurry at any point at the wet end of the paper machine. Alternatively, it may be applied from a tub size or at a size press or from showers to the dried or partially dried sheet.

The cationized dialdehyde polysaccharide dispersion prepared as above described has been found to be highly substantive to cellulosic fibers such that the addition of a salt such as aluminum sulfate is unnecessary where these dispersions are used. It is believed that the attractive forces between the electropositively charged macromolecules of cationized dialdehyde polysaccharide and the electronegatively charged fiber surfaces are of a sufficient magnitude to obviate the necessity for the use of any other substance.

The dialdehyde polysaccharides utilized in the process of this invention comprise a series of materials which are known to be capable of cross-linking cellulose. These materials may be generally described as polymeric dialdehydes, a preferred embodiment of which is dialdehyde starch. They are frequently referred to as periodate oxidized polysaccharides because of their preparation by the well known oxidation of polysaccharides with periodic acid. This preparation may be illustrated by the conversion of starch to dialdehyde starch or periodate oxidized starch using periodic acid in accordance with the following equation:



wherein n stands for the number of repeating structural units in the molecule, which may range from as few as about 20 to as many as several thousand. The preparation of dialdehyde starch is more particularly described in U.S. Patent No. 2,713,553, to Charles L. Mehlretter.

The dialdehyde polysaccharide to be used in the process of this invention may be the dialdehyde derivative of any polysaccharide such as corn, wheat, rice, tapioca or potato starches, amyloses, amylopectins, celluloses, gums, dextrans, algin, inulins and others. Of these polysaccharides, the dialdehyde derivatives of starch known generically as dialdehyde starch are the best known and most widely used. However, where it is desired to have derivatives of other polysaccharides, these may be used as well.

In general, it is preferred to use dialdehyde polysaccharides which are about from 90% to 100% oxidized, that is those wherein 90 to 100 of each 100 of the original anhydroglucose units have been converted to dialdehyde units such as by periodate oxidation as above described.

The cationizing agent may be characterized as a water soluble nitrogen-containing polymer which is electropositively charged in solution. There are a wide variety of such materials which are commercially available. For example, polyamides derived from polyalkylene polyamines and dicarboxylic acids may be used. A particularly preferred group of such materials is described in U.S. Patent No. 2,926,154, to Gerald I. Keim. The polyamides described in this patent are water soluble long chain polyamides containing the recurring groups:



wherein n and x are each 2 or more and R is the divalent organic radical of a dicarboxylic acid. The incorporation of epichlorohydrin into the polyamide chain results in the formation of water soluble cationic thermosetting resins. The amines which may be used in the formation of these polyamides include diethylenetriamine, triethylenetetramine, tetraethylenepentamine, dipropylenetriamine, and mixtures of polyethylene polyamines obtained by the reaction of ammonia with ethylene dichloride. In addition, there may be included aliphatic diamines such as ethylenediamine, propylenediamine, hexamethylenediamine and heterocyclic diamines such as piperazine or the like. The dicarboxylic acids which may be used include the saturated aliphatic dicarboxylic acids such as malonic, succinic, glutaric or adipic, and may also include diglycolic acid and blends of two or more of these dicarboxylic acids. In addition, the higher saturated aliphatic dicarboxylic acids such as azelaic and sebacic acids may be included.

Another series of cationizing agents which have been found effective in carrying out the process of this invention are complex polymeric water-soluble materials which are multistage reaction products of a nitrogenous compound such as dicyandiamide, acrylamide, urea, or guanidine and formaldehyde. A polycondensation product resulting from the reaction of dicyandiamide and formaldehyde has been found especially effective. The degree of polymerization may be kept under strict control so that a water-soluble condensate of low molecular weight forms. It is essential that no formation of insoluble matter is discernible in the water-soluble condensate subsequent to its standing at room temperature for several years.

Such product is a colorless, viscous liquid with the mold-like odor of formaldehyde. The material is readily dilutable with water, cationically active and chemically reactive. It imparts by itself no wet strength properties when added to aqueous fiber suspensions.

In addition to these specific exemplifications of cationizing agents which may be reacted with dialdehyde polysaccharides in accordance with the process of this invention, it is possible to use a wide variety of other materials as the cationizing agent so long as these essential requirements are met:

- (1) The material must be water soluble.
- (2) It must be polymeric in character.
- (3) It must contain nitrogen atoms which are available for interaction with the carbonyl groups of a dialdehyde polysaccharide.
- (4) It must be electropositive in character, that is, cationic, in solution.

The cationized dialdehyde polysaccharide dispersion may be added to any desired cellulosic material. More particularly, these dispersions may be added to a wide variety of cellulosic fibers or mixtures thereof. For example, any of the following as well as others may be successfully employed: unbleached kraft pulp, semi-bleached kraft pulp, bleached kraft pulp, unbleached sulfite pulp,

semi-bleached sulfite pulp, bleached sulfite pulp, unbleached semi-chemical pulp, semi-bleached semi-chemical pulp, bleached semi-chemical pulp, unbleached soda pulp, semi-bleached soda pulp, bleached soda pulp, unbleached and cooked cotton rag stock, semi-bleached and cooked cotton rag stock, bleached and cooked cotton rag stock, cooked bagasse fibers, either acid or alkali cooked cotton linter pulp of various types and grades, mechanical pulp from both coniferous and deciduous woods, cooked and semi-cooked hemp, sisal, ramie, jute, caroa and other bast fibers such as bamboo, palm and many grasses, old paper stock made up of any or all of any mixture of used papermaking fibers, cooked straw fibers, cooked flax fibers, and, in fact, any fibrous cellulosic material that lends itself to the formation of water laid cellulosic webs or form fabrics from an aqueous suspension of its fibers.

This invention will be better understood by reference to the following detailed examples which, however, are not to be considered as unduly limiting the scope of the instant invention, which is defined in the claims appended hereto.

EXAMPLE I

Dispersion preparation

A 5% dialdehyde polysaccharide dispersion using a water soluble cationic thermosetting polyamide resin as cationizing agent was prepared as follows:

A quantity of 900 ml. of tap water was adjusted to a total alkalinity of 100 p.p.m. (from 210 p.p.m.) using dilute sulfuric acid. The water was heated on a steam bath at 85° C. and 50 g. of periodate oxidized corn starch was added with stirring. The degree of oxidation of the periodate oxidized corn starch (dialdehyde starch) was 94% and the material had a moisture content of 9%. After 35 minutes of continued heating the slurry had thickened and thinned out upon 10 more minutes of heating. Then the pH of the dispersion was lowered to pH 3.5 using 5% sulfuric acid and 50 ml. of Kymene 557, a water soluble cationic thermosetting polyamide resin available from Hercules Powder Company, was added. Kymene 557 is supplied as an aqueous solution containing 10% active ingredients. The amount added corresponds to 10% on the weight of dialdehyde starch (solids basis). For complete interaction with the dialdehyde starch heating at 85° C. was continued for a period of 3 minutes. The reaction product was then cooled and the cationized dialdehyde starch dispersion was ready for use.

SHEET-MAKING PROCEDURE

The pulp was slurried in water to a consistency of 1% and the pH of the slurry was adjusted to pH 4.5-5.5 with dilute sulfuric acid. The required amount of pulp slurry to make 20 sheets was then withdrawn and treated with the cationized dialdehyde starch. After mixing thoroughly 250 ml. portions of the treated slurry were measured out for each 2.5 g. sheet and added to the pre-filled Deckle box of a Noble and Wood sheet machine. Water used to fill the deckle box was adjusted to a pH of 4.5-5.5. Pulp consistency in the deckle box was approximately 0.05%. After forming the sheet using a white water return system, the wet sheet was pressed with a felt press of the Noble and Wood machine to a consistency of approximately 32%. The sheet, still on the wire, was then dried at 220° F. during a three-minute drying cycle on the steam heated dryer of the sheet machine.

The blanks, in which no cationized dialdehyde starch was added were formed in the same manner, omitting the addition of the cationized dialdehyde starch.

TESTING OF HAND-SHEETS

The hand-sheets were tested for dry tensile strength and wet tensile strength using one-half inch strips over a four-inch span of the tensile tester. The wet and dry tensile data were converted to breaking length of paper ac-

cording to Tappi Standard T 220, T 404 and T 456. The data are shown in Table I below:

TABLE I

Hand-Sheet Material	Cationized dialdehyde starch added to oven dry (o.d.) pulp, percent	Wet Breaking Length, meters		Dry Breaking Length, meters	
		Off machine	Cured ¹	Off machine	Cured ¹
Northern Bleached Kraft, 450 cc. C.S.F.-----	0	211	364	7,363	7,370
	0.25	1,020	878	8,970	8,170
	0.50	1,190	1,470	8,907	9,000
	1.00	1,700	2,000	8,810	8,420
	2.50	2,590	3,470	9,087	9,860
Northern Unbleached Kraft, 450 cc. C.S.F.-----	0	334	486	7,310	8,480
	0.25	961	1,170	9,530	9,430
	0.50	1,210	1,330	9,180	9,270
	1.00	1,510	1,780	9,280	9,560
	2.50	2,540	2,590	10,400	10,300
Southern Unbleached Kraft, 450 cc. C.S.F.-----	0	283	320	5,850	6,000
	0.25	694	748	6,560	5,920
	0.50	937	1,120	6,600	5,800
	1.00	1,360	1,320	6,550	6,850
	2.50	1,610	1,940	7,020	7,640

¹ 105° C. for 10 minutes.

EXAMPLE II

A 5% dialdehyde starch dispersion using a water-soluble dicyandiamide-formaldehyde polycondensation product as cationizing agent was prepared in the same manner as described in Example I. The dicyandiamide-formaldehyde product was prepared as follows:

To a 50 gallon corrosion resistant kettle equipped with a recording thermometer, agitator, reflux condenser and a jacket or coil for cooling were charged 154.6 lb. of dicyandiamide, 248 lb. of 40% aqueous formaldehyde and 27.3 lb. of ammonium chloride. The slurry was heated at 30° C., at which point an exothermic reaction started. Within 30 to 40 minutes the temperature rose to 70° C. and all solid material was in solution. After the exothermic reaction came to a halt another 13.6 lb. of ammonium chloride was added. After 15 minutes the last part of the catalyst (13.6 lb.) was added and the mixture was stirred for three hours between 65° C. and 70° C. Then it was cooled. The total solids content was 67.5% (with catalyst), active ingredients 55.5%. Either 25 ml. or 50 ml. of a 30% solids containing solution of this dicyandiamide-formaldehyde-polycondensation product was added. This corresponds to 15% and 30% additions of cationizing agent on the weight of dialdehyde polysaccharide. The sheet making procedure and testing of the hand-sheets were the same as shown in Example I.

The results obtained are shown in Table II below:

TABLE II

Hand-Sheet Material, 450 cc. C.S.F.	Cationized dialdehyde starch added to oven dry (o.d.) pulp, percent	Wet breaking length, meters ¹				Dry breaking length, meters ¹			
		Off machine		Cured		Off machine		Cured	
		15%	30%	15%	30%	15%	30%	15%	30%
Northern bleached Kraft.	0	211	211	364	364	7,363	7,363	7,550	7,730
	0.25	760	1,290	823	1,360	8,200	8,037	8,830	8,560
	0.50	1,330	1,500	1,790	1,510	8,450	8,983	8,700	9,430
	1.00	1,753	1,876	2,620	3,080	8,790	9,307	9,970	9,690
	2.50	2,880	3,127	3,630	3,520	9,417	9,750	10,300	10,700
Northern Unbleached Kraft.	0	334	334	486	486	7,310	7,310	8,480	8,480
	0.25	1,220	1,220	1,450	1,450	8,710	8,710	9,820	9,820
	0.50	1,670	1,670	1,800	1,800	10,900	10,900	11,000	11,000
	1.00	2,000	2,000	2,600	2,600	10,300	10,300	10,700	10,700
	2.50	3,010	3,010	3,660	3,660	10,300	10,300	10,700	10,700

¹ Percent dicyandiamide-formaldehyde polycondensation product solids on weight of dialdehyde starch.

EXAMPLE III

A 9% dispersion of dialdehyde starch cooked in the presence of a buffer salt and cationized with Kymene 557 was prepared as follows:

Nine hundred milliliters of distilled water containing 10 g. of sodium acetate was heated at 60° C. One hundred grams of dialdehyde starch (assay 96%, moisture 8%) was added under stirring and the temperature kept at

60° C. until all granules were disrupted and a uniform dispersion formed. This took a total of 30 minutes.

Then 100 ml. of a 10% solution of Kymene 557 was added and the heating was continued for 3 minutes. The cationized dialdehyde starch dispersion was cooled and diluted to a solids content of 1% w/v.

Hand-sheets were formed in the same manner as described in Example I.

The following results shown in Table III below were obtained with a bleached kraft (450 cc. C.S.F.).

TABLE III

Hand-Sheet Material	Cationized dialdehyde starch added to o.d. pulp, percent	Wet breaking length (off machine), meters
Bleached Kraft, 450 cc. C.S.F.-----	0	360
	0.25	2,115
	0.50	2,310
	1.00	3,128
	2.00	3,554

In summary, this invention relates to cellulosic materials which have enhanced wet and dry strength and to a convenient process for their preparation. The process comprises treating cellulosic fibers with a reaction product of a dialdehyde polysaccharide and a cationizing agent which is:

1. Water soluble
2. Polymeric
3. Nitrogen-containing, and
4. Cationic in aqueous solution.

What is claimed is:

1. A process for improving the physical properties of cellulosic materials which comprises reacting an aqueous dispersion of a dialdehyde polysaccharide containing from about 1 to about 30 weight percent of the dialdehyde polysaccharide with a water-soluble polymeric nitrogen-containing cationizing agent selected from the class consisting of water-soluble polyamides derived from poly-

alkylene polyamines and dicarboxylic acids and dicyandiamide-formaldehyde polycondensation products at a pH of from about 3.0 to about 4.0 and a temperature of from about 60° C. to about 90° C. for a period of from about 1 minute to about 10 minutes, said cationizing agent being employed in an amount of from about 1 to about 50 weight percent based on the weight of the dialdehyde polysaccharide and adding the resulting cationized dialdehyde polysaccharide to an aqueous slurry of cellulosic fibers.

2. A process according to claim 1 wherein the cationizing agent is a water-soluble polyamide derived from polyalkylene polyamines and dicarboxylic acids.

3. A process according to claim 1 wherein the cationizing agent is a dicyandiamine-formaldehyde polycondensation product.

4. A process according to claim 1 wherein the dialdehyde polysaccharide is dialdehyde starch.

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