United States Patent Office

3,067,088

Patented Dec. 4, 1962

3,067,088

PROCESS FOR MAKING HIGH WET-STRENGTH PAPER CONTAINING POLYMERIC DIALDEHYDE

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No Drawing. Filed Mar. 24, 1960, Ser. No. 17,438
5 Claims. (Cl. 162—175)
(Granted under Title 35, U.S. Code (1952), sec. 266)

A nonexclusive, irrevocable, royalty-free license in the invention herein described, throughout the world for all purposes of the United States Government, with the power to grant sublicenses for such purposes, is hereby granted to the Government of the United States of America.

This invention relates to a process for producing improved wet-, dry-, burst-, and fold-strengths, and improved water resistance in cellulosic fiber paper by adding to the stock both a periodate oxidized polysaccharide and a polymeric nitrogen containing compound. The process comprises incorporating in the paper stock slurry prior to sheet formation a periodate-oxidized polysaccharide, preferably dialdehyde starch, and a positively charged nitrogen containing starch product that attaches itself to the negatively charged cellulosic fiber by electrical attraction and simultaneously precipitates and coagulates the dialdehyde starch intimately on and in the cellulosic fiber structure. By this means high retention of dialdehyde starch in the fibers is obtained with increased efficiency of cross-bonding of the fibers by the aldehyde groups in the dialdehyde starch to produce high wet-strength paper of improved dry tensile and burst strengths.

The commercially available nitrogen-containing agents of this invention are not themselves effective in producing wet strength in paper as are the melamine-formaldehyde resins and urea-formaldehyde resins, nor are dialdehyde starch and its aqueous dispersions by themselves of value as wet-strength imparting agents when applied prior to sheet formation.

This application is a continuation-in-part of copending application, Serial No. 858,836, filed December 10, 1959. The said copending application discloses the production of high wet-strength paper by addition of partially hydrolyzed dialdehyde starch and of alum (aluminum sulfate) to the paper stock. Paper of high wet strength and improved dry strength is obtained by this treatment of cellulosic pulp. The high concentrations of papermaker's alum employed, however, increases the corrosiveness of stock systems with a reduction of the life of mechanical equipment, and places a limitation on the type of equipment that can be used.

We have now discovered that paper of high wet strength and improved dry, burst, and fold strengths and improved water resistance is obtained when polymeric nitrogen containing compounds such as amino-starches are used in conjunction with partially depolymerized dialdehyde starch as additives to pulp prior to sheet formation. Fixation on the pulp is extremely rapid and extended curing is unnecessary. The additives of the present invention permit the production of wet-strength papers which are completely free of alum. However, alum need not be completely eliminated from stock containing dialdehyde starch and polymeric cationic nitrogen containing products. A judicious combination of polymeric nitrogen-containing products and alum in more practical low concentrations also produces good wet strength in paper and improved dry tensile strength, burst strength, and water resistance when used with dialdehyde starch at the beater stage or other stages of papermaking prior to sheet formation.

The use of dialdehyde starch with such smaller additions of aluminum sulfate in the absence of the nitrogen containing polymeric cationic agents produces paper with much lower wet strength as will be shown hereinafter.

The polymeric dialdehyde obtained by controlled partial degradative hydrolysis (e.g., by mild heating in weak bisulfite solution) of substantially fully periodate-oxidized starch so that a major portion of the polymer units are in the molecular weight range of about 300,000 to about 5,000,000, as shown in the said copending application, are necessary for obtaining the improvement of the present invention. Obviously, dialdehyde starch which has been molecularly degraded to similar extents by other known means would also be operative.

The cationic additives comprise water soluble or water dispersible polymers containing nitrogen substituents which give the polymers a positive charge. An example of such polymers which are particularly related to the invention are the commercially available cationic starches which contain primary, secondary, tertiary or quaternary amino-groups in the starch molecule. These primary, secondary, and tertiary amino-starches have the general chemical formula

$$\begin{array}{c} R' \\ | \\ R^2\text{—}N\text{—}R\text{—}OZ \end{array}$$

wherein Z is a radical derived from starch through ether formation, R is an alkylene or hydroxyalkylene radical, R′ is an alkyl radical or hydrogen radical, and R^2 is an alkyl or hydrogen radical.

By reaction of the tertiary amine-substituted starch with alkyl halides, commercially available quaternary amine-substituted starches are formed or quaternary amines may be reacted directly with starch. Such quaternary amine starches are also capable of preparation by other means and have this general formula

$$\left[\begin{array}{l} R' \\ \quad \diagdown \\ \qquad N\text{—}R\text{—}OZ \\ \quad \diagup\ | \\ R^3\ R^3 \end{array}\right]^+ X^-$$

wherein R^3 is an alkyl radical and X is an anion selected from the group consisting of hydroxyl, chloride, iodide, or sulfate, and wherein Z, R, R′, and R^2 are the same as in the previous formula.

However, our invention is applicable to all cationic polymeric nitrogen-containing compounds such as polymeric amidazolines, polyalkylene polyamines and the like, which are water soluble or water dispersible, or which can readily be made water soluble or water dispersible, and which are substantive to cellulosic fibers.

The amount of positively charged nitrogen-containing polymers that may be used in accordance with our invention is about 0.5 to 5 percent based on the weight of the cellulosic fiber. It is not economically advantageous to use more than 5 percent of the agent. Monomeric amines are not effective for the purpose of this invention.

The chemical additives of the present invention, while useful in the manufacture of all types of paper, will find particular use in the production of paper products where high wet and dry strengths and reduced water absorption are desired.

The cellulosic pulp may consist of any of the common paper fibers such as bleached and unbleached sulphate and sulphite pulps and blends of these, and the invention also relates to felted fibrous cellulosic materials such as board, shaped pulp articles and the like.

The invention is illustrated further by means of the following examples.

EXAMPLE 1

Dialdehyde starch produced by oxidation of starch to the extent of 95 percent with periodate was dispersed and partially degrated so that the polymer size distribution was in the range of 300,000 to 5,000,000 by heating a 3 percent dispersion of the dialdehyde starch in a 0.45 percent aqueous solution of sodium bisulfite at 90 to 95° C. for approximately 40 minutes. The partially hydrolyzed dialdehyde starch dispersion was added to and mixed with bleached paper pulp suspended in water after the addition thereto of a commercial cationic starch having the formula

$$C_2H_5-\overset{C_2H_5}{\overset{|}{N}}-CH_2-CH_2-OZ$$

wherein Z is the radical derived from starch through ether formation. The cationic starch and dialdehyde starch were incorporated in handsheets through wet-end addition to the pulp, the handsheets of which were then tested for dry and wet tensile strength, dry burst strength, fold endurance, and water absorbency. Tensile strength values are expressed as pounds per inch width. Wet tensile strength is given for a 30-minute soaking period at 23° C. in distilled water. Thus, 340 milliliters of a tap water slurry (344 p.p.m. as $CaCO_3$) containing 1.2 grams (dry basis) of bleached sulfate pulp having a Schopper-Riegler freeness of 700 ml. were adjusted to approximately pH 6 with hydrochloric acid. To the slurry were added 5 ml. of an aqueous dispersion containing 0.030 g. of the cationic starch and the pH was adjusted to approximately 4.5 with hydrochloric acid. One ml. of the 0.45 percent aqueous solution of sodium bisulfite containing 0.030 g. of the partially degrated dialdehyde starch were then introduced to the fiber slurry and the furnished stirred for 2 minutes. Sheets were then formed on the wire using diluent water at pH 4.5 and dried according to the TAPPI standard procedure.

The resulting sheets had the same feel and appearance as before the treatment and displayed high wet tensile strength, improved dry tensile and burst strengths and reduced water absorbency. The strength values of the treated sheets are shown in Table I in comparison to the untreated sheets and sheets treated with dialdehyde starch alone and cationic starch alone.

The quantities of dialdehyde starch and cationic starch used in this example are 2.5 percent of the dry fiber weight. The cationic starch used was the commercially available starch ether produced by reaction of β-diethylamine ethyl chloride and starch according to U.S. Patent No. 2,813,093.

Table I

Dialdehyde starch, percent		Cationic starch, percent		Tensile strength, lbs./in.		Burst strength, pts./100 lbs.	Absorbancy Cobb, g./sq. m.-min.
Added	In sheet	Added	In sheet	Dry	Wet		
0	0	0	0	28.4	0.8	137	169
2.5	0.34	0	0	32.2	2.5	-------	-------
0	0	2.5	1.34	35.4	1.3	163	-------
2.5	0.52	2.5	1.28	37.0	7.9	174	115

EXAMPLE 2

This example illustrates the improvement of properties obtained with another commercially available nitrogen containing cationic starch in conjunction with dialdehyde starch. This cationic starch was prepared by reaction of epichlorohydrin with trimethylamine followed by reaction of this product with starch as described in U.S. Patent No. 2,876,217, and has the structure

$$\left[CH_3-\underset{CH_3}{\overset{CH_3}{N}}-CH-\underset{OH}{CH}-CH_2-OZ\right]^+Cl^-$$

where Z is the radical derived from starch.

The procedure used for the preparation of the hand sheets was identical to that used in Example 1. The resulting sheets had the same feel and appearance as the untreated paper and showed surprisingly high wet and dry tensile strength, and improved Mullen burst strength.

EXAMPLE 3

This example illustrates the improvement in dry and wet tensile strength, Mullen burst strength, and Schopper fold endurance in paper prepared by addition of 2.5 percent of dialdehyde starch and 1.0 percent of cationic starch of Example 1 based on the dry fiber weight under the conditions of application described in Example 1. The resulting sheets had the same appearance as the paper prepared with untreated cellulosic pulp and showed improved properties as shown in Table II.

Table II

Dialdehyde starch, percent		Cationic starch, percent		Tensile strength, lbs./in.		Burst strength, pts./100 lbs.	Schopper fold
Added	In sheet	Added	In sheet	Dry	Wet		
0	0	0	0	28.4	0.8	137	1,400
0	0	1.0	0.30	32.8	0.9	137	1,570
2.5	0.36	1.0	0.28	37.3	5.0	153	2,200

EXAMPLE 4

This example illustrates the variation in concentrations of dialdehyde starch and cationic starch that can be used in the treatment of pulp prior to sheet formation to produce sheets of high wet strength and improved dry strength.

Three hundred and forty milliliters of tap water slurry containing 1.2 g. (dry basis) of a bleached softwood sulfate pulp (S.R. freeness 700 ml.) were adjusted to pH 6 with hydrochloric acid. To the slurry was added from 0.006 g. to 0.060 g. (0.5 to 5 percent of the dry weight of the pulp) of cationic starch of Example 1 which had been dispersed in water by heating prior to use. The pH of the slurry was then adjusted to pH 4.5 with hydrochloric acid and an aqueous bisulfite dispersion of dialdehyde starch containing from 0.012 g. to 0.060 g. of the dialdehyde starch (1 to 5 percent of the dry fiber weight) was then introduced to the fiber slurry and the furnish stirred for 2 minutes. Sheets were then formed and dried according to the Tappi standard procedure. Table III shows the increased strengths obtained using different proportions of dialdehyde starch and cationic starch within the range 0.5 percent to 5 percent of the dry fiber weight.

Table III

Dialdehyde starch, percent		Cationic starch, percent		Tensile strength, lbs./in.		Burst strength, pts./100 lbs.
Added	In sheet	Added	In sheet	Dry	Wet	
0	0	0	0	28.4	0.8	137
0.5	0.14	1.0	0.35	35.8	3.6	153
1.0	0.25	1.0	0.16	34.3	4.2	158
2.0	0.35	1.0	0.38	35.8	5.0	151
0.5	0.21	2.5	1.41	37.8	4.9	159
1.0	0.30	2.5	1.20	38.1	5.6	161
2.0	0.52	2.5	1.25	38.1	8.1	160
2.0	0.69	5.0	3.19	44.0	9.3	153
5.0	0.94	5.0	2.53	41.8	10.2	175

Having disclosed our invention, we claim:

1. The process of producing paper of high wet strength from cellulosic fibers, comprising the steps of adding to an aqueous suspension of cellulosic fibers an aqueous dispersion containing 0.5 to 5 percent based on the dry weight of the cellulosic fibers of a cationic starch member se-

lected from the group consisting of a starch of the formula

$$(C_2H_5)_2N-CH_2-CH_2-OZ$$

and a starch of the formula

$$\left[CH_3-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{N}}}}-CH_2-\underset{OH}{\underset{|}{CH}}-CH_2-OZ\right]^+Cl^-$$

wherein Z is the radical derived from starch through ether formation, adjusting the pH to about 4.5, adding an aqueous bisulfite dispersion containing 0.5 to 5 percent of dialdehyde starch based on the dry weight of the cellulosic fibers, the dialdehyde starch further being substantially fully periodate-oxidized starch that has been partially depolymerized by bisulfite to substantially the molecular weight range of about 300,000 to about 5,000,000, forming the cellulosic fibers so treated into a waterlaid sheet, and drying the resulting sheet.

2. A process as in claim 1 wherein the cationic starch has the formula

$$C_2H_5-\underset{C_2H_5}{\underset{|}{N}}-C_2H_4-OZ$$

where Z is the radical derived from starch through ether formation.

3. A process as in claim 1 wherein the cationic starch has the formula

$$\left[(CH_3)_3N-CH_2-\underset{OH}{\underset{|}{CH}}-CH_2-OZ\right]^+Cl^-$$

where Z is the radical derived from starch through ether formation.

4. The process of producing paper of high wet strength from cellulosic fibers comprising adding to an aqueous suspension of cellulosic fibers an aqueous dispersion of a cationic starch selected from the group consisting of

$$R^2-\overset{R^1}{\overset{|}{N}}-R-OZ$$

and

$$\left[R^1R^2\underset{R_3}{\underset{|}{N}}-R-OZ\right]^+X^-$$

where Z is a radical derived from starch through ether formation, R is a member of the group consisting of alkylene and hydroxyalkylene, R^1 is a member of the group consisting of alkyl and hydrogen, R^2 is a member of the group consisting of alkyl and hydrogen, R^3 is alkyl, and X is an anion from the group consisting of hydroxyl, chloride, iodide, and sulfate, adding to said suspension an aqueous bisulfite suspension containing up to about 5% based on the dry weight of the cellulosic fibers of a substantially fully periodate-oxidized starch that has been partially depolymerized by bisulfite to a molecular weight of about from 300,000 to 5,000,000, forming the cellulosic fibers into a waterlaid sheet, and drying the resulting sheet.

5. A product particularly suitable for use in the manufacture of paper and felted cellulosic materials of high wet strength, comprising cellulosic fibers suspended in water acidified to about pH 4.5, said fibers also containing a cationic starch and also a bisulfite partially degraded substantially fully periodate-oxidized starch adsorbed thereon, the major portion of said bisulfite partially degraded periodate-oxidized starch having a molecular weight in the range of about 300,000 to about 5,000,000.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,067,088

December 4, 196

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It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 47, for "amidazolines" read -- imidazolines --.

Signed and sealed this 14th day of April 1964.

(SEAL)
Attest:
ERNEST W. SWIDER

Attesting Officer

EDWARD J. BRENNER

Commissioner of Patents