United States Patent Office 2,926,116 Patented Feb. 23, 1960

2,926,116

WET-STRENGTH PAPER AND METHOD OF MAKING SAME

Gerald I. Keim, West Grove, Pa., assignor to Hercules Powder Company, Wilmington, Del., a corporation of Delaware

No Drawing. Application September 5, 1957 Serial No. 682,086

10 Claims. (Cl. 162—164)

This invention relates to the manufacture of resin-treated cellulosic fibers and fibrous products prepared therefrom and is directed particularly to a method for improving the wet strength of felted fibrous cellulosic materials such as paper, paperboard, shaped paper articles and the like. The invention includes the improved cellulosic fibers and fibrous products themselves as well as methods of preparing these products from aqueous suspensions of fibrous cellulosic material such as paper pulp.

Commercial wet-strength resins presently available do not function effectively at pH's much above 5.5. As a consequence, many grades of paper made on the alkaline side for various reasons such as strength, softness, use of alkaline fillers and so on, cannot be wet-strengthened. Moreover, the low pH required to effectively use the acid-curing wet-strength resins presently available increases machine corrosion and raises maintenance costs.

A principal object of the present invention is the provision of a method for adding wet-strength to any type of paper regardless of whether it is produced under acid, neutral or alkaline conditions.

In accordance with the invention, the above and other objects are accomplished by applying to fibrous cellulosic material such as paper pulp an uncured thermosetting cationic resin comprising a water-soluble polymeric reaction product of epichlorohydrin and a polyamide derived from a polyalkylene polyamine and a saturated aliphatic dibasic carboxylic acid containing from about 3 to 10 carbon atoms. It has been found that resins of this type impart wet-strength to paper whether made under acid, alkaline or neutral conditions. Moreover, such resins are substantive to cellulosic fibers so that they may be economically applied thereto while the fibers are in dilute aqueous suspensions of the consistency used in paper mills.

In the preparation of the cationic resins contemplated for use herein, the dibasic carboxylic acid is first reacted with the polyalkylene polyamine, preferably in aqueous solution, under conditions such as to produce a water-soluble polyamide containing the recurring groups

$$—NH(C_nH_{2n}HN)_x—CORCO—$$

where n and x are each 2 or more and R is the divalent hydrocarbon radical of the dibasic carboxylic 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 the resins of the invention are the saturated aliphatic dibasic carboxylic acids containing from 3 to 10 carbon atoms such as succinic, adipic, azelaic and the like. The saturated dibasic acids having from 4 to 8 carbon atoms in the molecule are preferred. Blends of two or more of the saturated dibasic 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, and dipropylenetriamine, 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 th 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 dibasic 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 dibasic 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 dibasic 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 do not produce efficient wet-strength resins when reacted with epichlorohydrin.

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. This will create an environment favoring the conversion of the chlorohydrin groups to epoxide groups, thereby increasing the ratio of the latter to the former.

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 mol 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 cationic polyamide-epichlorohydrin resins, prepared as herein described, may be applied to paper or other felted cellulosic products by tub application or by spraying, if desired. Thus, for example, preformed and partially or completely dried paper may be impregnated by immersion in, or spraying with, an aqueous solution of the resin following which the paper may be heated for about 0.5 to 30 minutes at temperatures of 90° C. to 100° C. or higher to dry same and cure the resin to a water-insoluble condition. The resulting paper has greatly increased wet strength, and, therefore, this method is well suited for the impregnation of paper towels, absorbent tissue and the like as well as heavier stocks such as wrapping paper, bag paper and the like to impart wet strength characteristics thereto.

The preferred method of incorporating these resins in paper, however, is by internal addition prior to sheet formation whereby advantage is taken of the substantivity of the resins for hydrated cellulosic fibers. In practicing this method, an aqueous solution of the resin in its uncured and hydrophilic state is added to an aqueous suspension of paper stock in the beater, stock chest, Jordan engine, fan pump, head box or at any other suitable point ahead of sheet formation. The sheet is then formed and dried in the usual manner, thereby curing the resin to its polymerized and water-insoluble condition and imparting wet strength to the paper.

The cationic thermosetting resins herein disclosed impart wet strength to paper when present therein in amounts of about 0.1–5% or more based on the dry weight of the paper. The quantity of resin to be added to the aqueous stock suspension will depend on the degree of wet strength desired in the finished product and on the amount of resin retained by the paper fibers.

The uncured cationic thermosetting resins of the invention, incorporated in paper in any suitable manner, as described above, may be cured under acid, neutral or alkaline conditions, i.e., at pH's from about 4.0 to 10, by subjecting the paper to a heat-treatment for about 0.5 to 30 minutes at a temperature from about 90 to 100° C. Optimum results, however, are obtained under alkaline conditions. In view of this, and the rather extensive corrosion of equipment encountered at pH's below about 6.0, it is preferred to carry out the curing step at a pH from about 6.0 to about 9.0.

The following examples will illustrate the invention.

EXAMPLE 1

Two hundred twenty-five grams (2.18 moles) of diethylenetriamine and 100 grams of water were placed in a 3-necked flask equipped with a mechanical stirrer, thermometer and condenser. To this was added 290 grams (2.0 moles) of adipic acid. After the acid had dissolved in the amine, the solution was heated to 185–200° C. and held there for 1½ hours. Then vacuum from a water pump was applied to the flask during the period required for the contents of the flask to cool to 140° C. following which 430 grams of H_2O was added. The polyamide solution contained 52.3% solids and had an acid number of 2.1.

To 60 grams of this polyamide solution in a round-bottom flask were added 225 grams of H_2O. This solution was heated to 50° C. and 12.5 grams of epichlorohydrin were added dropwise over a period of 11 minutes. The contents of the flask was then heated to 60–70° C. until it had attained a Gardner viscosity of >E. Then 150 grams of H_2O were added to the product, and it was cooled to 25° C. Eleven mls. of 3.7% HCl were then added to adjust the pH to 5.0. The product contained 9.0% solids and had a Gardner viscosity of C–D.

Tacoma-bleached kraft was beaten to a Schopper-Riegler freeness of 750 cc. in a Noble and Wood cycle beater. The pulp was then adjusted to pH 9.0 with 10% NaOH and 1.0%, based on the dry weight of pulp, of the polyamide-epichlorohydrin resin, prepared as described, was added. The pulp was sheeted on a Noble and Wood handsheet machine using a closed system in which the white water contained 100 p.p.m. sulfate ion and had been adjusted to pH 9.0 with 10% NaOH. A portion of the resulting handsheets were given an additional cure of 1 hour at 105° C. The sheets were then soaked in distilled water for 2 hours and tested for wet strength. Results are listed in the table which follows Example 4.

EXAMPLE 2

A polyamide was prepared from 319 grams (2.18 moles) of triethylenetetramine and 290 grams (2.0 moles) of adipic acid according to the procedure described in Example 1. The polyamide solution had a pH of 10.8, an acid number of 3.2 and contained 4.98% solids.

Sixty-three grams of the polyamide solution was dissolved in 225 grams of H_2O. This solution was stirred mechanically and heated to 50° C. Twenty-five grams of epichlorohydrin were added dropwise over a period of three minutes. The solution was then heated to 60–70° C. until it reached a viscosity of E (Gardner). Then it was diluted with 225 grams of H_2O, cooled to 25° C. and adjusted to pH 5.0 with 11 ml. of 3.7% HCl. The product containing 8.4% solids and having a Gardner viscosity of <C, was evaluated in bleached kraft pulp according to the procedure presented in Example 1. Results are listed in the table following Example 4.

EXAMPLE 3

A polyamide was prepared according to the procedure given in Example 1 using 225 grams (2.18 moles) of diethylenetriamine and 218 grams (1.5 moles) of adipic acid and 94 grams (0.5 mole) of azelaic acid. Fifty-seven and one-half grams of the polyamide solution (55% solids) were dissolved in 115 grams of H_2O and heated to 50° C. To this were added 15 grams of epichlorohydrin over a period of 6 minutes. This solution was then heated at 60–70° C. until the viscosity of the condensate reached >E (Gardner). Then 150 grams of H_2O were added and the product was cooled to 25° C. It was adjusted to pH 5.0 by adding 10 ml. of 3.7% HCl. The finished resin had a viscosity of B (Gardner) and contained 9.5% solids. It was evaluated in paper according to the procedure outlined in Example 1. Results are listed in the table following Example 4.

EXAMPLE 4

Sheets of paper were prepared and tested for wet

strength, as in Example 1, except that no resin was incorporated. The results are set forth in the following table.

Table

Example	Percent Resin Added Based on Dry Pulp	Basis Weight, lb./3,000 sq. ft.	Wet Tensile, lb./in.	Wet Tensile Cured, lb./in.
1	1.0	40.6	6.5	8.5
2	1.0	39.2	5.9	8.6
3	1.0	40.3	6.0	8.2
4	1.0	40.8	7.4	8.7
5	0.0	40.5	0.2	1.1

The following additional example will further illustrate the invention where a portion of the polyalkylene polyamine utilized in preparing the resin is replaced by a diamine.

EXAMPLE 5

A polyamide was prepared from the following ingredients:

Diethylenetriamine..... 204.4 grams (1.98 moles).
Ethylenediamine..... 14.0 grams (0.24 mol).
Adipic acid..... 290.0 grams (1.98 moles).
Water..... 100.0 grams.

The procedure of Example 1 was followed with the following exceptions. (1) The reaction mixture was held between 180° C. and 195° C. for 45 minutes; (2) aspirator vacuum was used during this entire period; and (3) the mixture was cooled to 140° C. and diluted with 430 ml. of distilled water (80° C.). The polyamide solution contained 52.4% total solids and had an acid number of 3.4.

To 60.5 grams of this polyamide solution were added 225.0 grams of H_2O. This solution was heated to 50° C. and 11.25 grams of epichlorohydrin was added dropwise over a period of about 11 minutes. The solution was then heated to 70–80° C. and held at this temperature until it had attained a viscosity of E Gardner-Holdt. It was then diluted with 173 ml. of water and adjusted to pH 5.0 with dilute HCl. The product contained 8.9% solids and had a Gardner viscosity of B–C.

Tacoma bleached kraft waterleaf sheets were tubsized (30-second dip) in a 2.0% aqueous solution of the resin, prepared as above described, and adjusted to pH 9.0 with 10% sodium hydroxide. The sheets were squeezed (roll) and drum dried. Half were cured at 105° C. for one hour and the cured and uncured sheets then soaked in distilled water for 2 hours and tested for Mullen burst. The Mullen burst (pounds per square inch-average of five determinations) was 10.8 for the uncured sheets and 15.2 for the cured sheets as compared with a Mullen burst of less than 1 for sheets which had not been treated with the resin.

It will thus be seen that the present invention makes it possible to prepare wet-strength paper under acid, neutral or alkaline conditions and by internal addition or by surface application. While preferred embodiments of the invention have been exemplified and described herein, the invention is not to be construed as limited thereby except as the same may be included in the following claims.

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

1. A process for the production of wet-strength paper which comprises incorporating therein from about 0.1% to about 5%, based on the weight of the paper, of a cationic thermosetting resin, said resin comprising a water-soluble reaction product of epichlorohydrin and a polamide containing secondary amine groups, the ratio of epichlorohydrin to secondary amine groups of said polyamide being from about 0.5 to 1 to about 1.8 to 1, said polyamide being obtained by heating together at a temperature from about 110° C. to about 250° C. a C_3–C_{10} saturated aliphatic dibasic carboxylic acid and a polyalkylene polyamine in a mole ratio of polyalkylene polyamine to dibasic acid of from about 0.8 to 1 to about 1.4 to 1, and then curing the resin to a water-insoluble state.

2. A process for the production of wet-strength paper which comprises adding to an aqueous suspension of cellulosic paper stock a water-soluble cationic thermosetting resin formed by reacting epichlorohydrin with a polyamide of a C_3–C_{10} saturated aliphatic dibasic carboxylic acid and from about 0.8 to about 1.4 moles, per mole of dibasic acid, of a polyalkylene polyamine at a temperature from about 45° C. to about 100° C., said polyamide containing secondary amine groups, the ratio of epichlorohydrin to secondary amine groups of said polyamide being from about 0.5 to 1 to about 1.8 to 1, adsorbing from about 0.1–5% of said resin on said paper stock, forming the stock so treated into a sheet, and heating the sheet to cure the resin to a water-insoluble state.

3. A process for the production of wet-strength paper which comprises adding to an aqueous suspension of cellulosic paper stock a water-soluble cationic thermosetting resin formed by reacting, at a temperature from about 45° C. to about 100° C., epichlorohydrin with a polyamide of a C_3–C_{10} saturated aliphatic dibasic carboxylic acid, from about 0.8 to about 1.4 moles, per mole of dibasic acid, of a polyalkylene polyamine and an aliphatic diamine, the amount of said aliphatic diamine not exceeding 50% by weight of the polyalkylene polyamine, said polyamide containing secondary amine groups, the ratio of epichlorohydrin to secondary amine groups of said polyamide being from about 0.5 to 1 to about 1.8 to 1, adsorbing from about 0.1–5% of said resin on said paper stock, forming the stock so treated into a sheet, and heating the sheet to cure the resin to a water-insoluble state.

4. A process for the production of wet-strength paper which comprises incorporating therein from about 0.1% to about 5%, based on the dry weight of the paper, of a cationic thermosetting polyamide-epichlorohydrin resin obtained by (1) reacting a C_3–C_{10} saturated aliphatic dibasic carboxylic acid with from about 0.8 to about 1.4 moles, per mole of dibasic carboxylic acid, of a polyalkylene polyamine at a temperature from about 110° C. to about 250° C. to form a polyamide containing secondary amine groups and (2) reacting the polyamide with epichlorohydrin at a temperature from about 45° C. to about 100° C. and at a ratio of epichlorohydrin to secondary amine groups of the polyamide of from about 0.5 to 1 to 1.8 to 1 to form a water-soluble cationic thermosetting resin, said resin having been cured to a water-insoluble state.

5. A process for the production of wet-strength paper which comprises incorporating therein from about 0.1% to about 5%, based on the dry weight of the paper, of a cationic thermosetting polyamide-epichlorohydrin resin obtained by (1) reacting a C_3–C_{10} saturated alyphatic dibasic carboxylic acid with a polyalkylene polyamine in a mole ratio of polyalkylene polyamine to dibasic acid of from about 0.8 to 1 to about 1.4 to 1 and at a temperature from about 160° C. to about 210° C. to form a polyamide containing secondary amine groups, and (2) reacting the polyamide with epichlorohydrin at a temperature from about 45° C. to about 70° C. and in a ratio of epichlorohydrin to secondary amine groups of said polyamide of from about 0.5 to 1 to about 1.8 to 1, and then curing the resin to a water-insoluble state.

6. A paper product having improved wet strength comprising sheeted cellulosic fibers containing from about 0.1% to 5%, based on its dry weight, of a cationic thermosetting resin, said resin comprising a water-soluble reaction product of epichlorohydrin and a polyamide containing secondary amine groups, the ratio of epichlorohydrin to secondary amine groups of said poly-

amide being from about 0.5 to 1 to about 1.8 to 1, said polyamide being obtained by heating together at a temperature from about 110° C. to about 250° C. a C_3–C_{10} saturated aliphatic dibasic carboxylic acid and from about 0.8 to about 1.4 moles, per mole of dibasic acid, of a polyalkylene polyamine, said resin having been cured to a water-insoluble state.

7. A paper product having improved wet strength comprising sheeted cellulosic fibers containing from about 0.1% to 5%, based on its dry weight, of a cationic thermosetting polyamide-epichlorohydrin resin obtained by (1) reacting a C_3–C_{10} saturated aliphatic dibasic carboxylic acid with from about 0.8 to about 1.4 moles, per mole of dibasic acid, of a polyalkylene polyamine at a temperature from about 110° C. to about 250° C. to form a polyamide containing secondary amine groups and (2) reacting the polyamide with epichlorohydrin at a temperature from about 45° C. to about 100° C. and at a ratio of epichlorohydrin to secondary amine groups of the polyamide of from about 0.5 to 1 to 1.8 to 1 to form a water-soluble cationic thermosetting resin, said resin having been cured to a water-insoluble state.

8. A paper product having improved wet strength comprising sheeted cellulosic fibers containing from about 0.1% to 5%, based on its dry weight, of a cationic thermosetting polyamide-epichlorohydrin resin obtained by (1) reacting a C_3–C_{10} saturated aliphatic dibasic carboxylic acid with a polyalkylene polyamine in a mole ration of polyalkylene polyamine to dibasic acid of from about 0.8 to 1 to about 1.4 to 1 and at a temperature from about 160° C. to about 210° C. to form a polyamide containing secondary amine groups, and (2) reacting the polyamide with epichlorohydrin at a temperature from about 45° C. to about 70° C. and in a ratio of epichlorohydrin to secondary amine groups of said polyamide of from about 0.5 to 1 to about 1.8 to 1.

9. A process in accordance with claim 5 in which the dibasic carboxylic acid is a C_4–C_8 saturated aliphatic dibasic carboxylic acid.

10. A paper product in accordance with claim 8 in which the dibasic carboxylic acid is a C_4–C_8 saturated aliphatic dibasic carboxylic acid.

References Cited in the file of this patent

UNITED STATES PATENTS

2,595,935	Daniel et al.	May 6, 1952

FOREIGN PATENTS

529,729	Canada	Aug. 28, 1956
610,311	Great Britain	Oct. 14, 1948

OTHER REFERENCES

Serial No. 323,512, Hagedorn (A.P.C.), published April 20, 1943.

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,926,116 February 23, 1960

Gerald I. Keim

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

Column 2, line 30, for "th" read -- the --; column 8, lines 1 and 2, for "ration" read -- ratio --.

Signed and sealed this 23rd day of August 1960.

(SEAL)
Attest:

KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents