WET-STRENGTH PAPER AND METHOD OF MAKING SAME

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

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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 polyaikylene polycarboxylic acid and employed as an 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 polyaikylene polycarboxylic acid, preferably in aqueous solution, under conditions such as to produce a water-soluble polycarboxylic acid containing the recurring groups

\[-\text{NH(CH}_2\text{H}_2\text{N)}_\text{x}]\text{CORCO—}\]

where \(n\) and \(x\) are each 2 or more and \(R\) is the divalent hydrocarbon radical of the dibasic carboxylic acid. This water-soluble polycarboxylic acid 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 acid 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 polyaikylene polycarboxylic acids including polyethylene polycarboxylic acids, polypropylene polycarboxylic acids, polybutylene polycarboxylic acids and so on may be employed of which the polyethylene polycarboxylic acids represent an economically preferred class. More specifically, the polyaikylene polycarboxylic acids contemplated for use may be represented as polycarboxylic acids in which the nitrogen atoms are linked together by groups of the formula \(\text{—C}_n\text{H}_{2n—2}\text{—}\) 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 \(\text{—C}_n\text{H}_{2n—2}\text{—}\) or to carbon atoms further apart, but not to the same carbon atom. This invention contemplates not only the use of such polycarboxylic acids as diethylenetriamine, triethylenetetramine, tetraethylenepenta-
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 chloroformation of 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 to at least to 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 cationic polyamide-epichlorohydrin resins, prepared as herein described, may be applied to paper by a number of methods, e.g., by brushing, spraying, or by spraying if desired. Thus, for example, preformed and partially or completely dry 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 120° C. to further dry 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 suspension 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 0.1-3% 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 10, 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, ther-
strength, as in Example 1, except that no resin was incorporated. The results are set forth in the following table.

Table

<table>
<thead>
<tr>
<th>Example</th>
<th>Percent. Resin</th>
<th>Basis Weight, lb.</th>
<th>Wet Tensile Curved, lb./in.</th>
<th>Wet Tensile Straight, lb./in.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0</td>
<td>40.6</td>
<td>6.5</td>
<td>8.5</td>
</tr>
<tr>
<td>2</td>
<td>1.0</td>
<td>28.2</td>
<td>6.9</td>
<td>8.6</td>
</tr>
<tr>
<td>3</td>
<td>1.0</td>
<td>40.3</td>
<td>6.0</td>
<td>8.2</td>
</tr>
<tr>
<td>4</td>
<td>1.0</td>
<td>40.8</td>
<td>7.4</td>
<td>8.7</td>
</tr>
<tr>
<td>5</td>
<td>6.0</td>
<td>40.6</td>
<td>6.0</td>
<td>8.1</td>
</tr>
</tbody>
</table>

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

EXEMPLARY EXAMPLE 5

A polyamide was prepared from the following ingredients:

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight (gms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diethylenetriamine</td>
<td>204.4 gms (1.98 moles)</td>
</tr>
<tr>
<td>Ethylenediamine</td>
<td>146.9 gms (0.24 mol)</td>
</tr>
<tr>
<td>Adipic acid</td>
<td>290.0 gms (1.98 moles)</td>
</tr>
<tr>
<td>Water</td>
<td>100.0 gms</td>
</tr>
</tbody>
</table>

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 H₂O. This solution was heated to 50° C. and 11.25 grams of epichlorohydrin was added drop-wise 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-Hold. It was then diluted with 173 ml. of water and adjusted to pH 5.0 with dilute HCl. The product contained 85.9% solids and had a Gardner viscosity of B-C.

Talcum bleached kraft waterleaf sheets were tub-sized (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 dry weight of the paper, of a cationic thermosetting resi- in.

2. A process for the production of wet-strength paper which comprises adding to an aqueous suspension of cellulose paper stock a water-soluble cationic thermosetting resin formed by reacting epichlorohydrin with a polyamide of a C₆-C₉ saturated aliphatic diacid carboxylic acid and from about 0.8 to about 1.4 moles, per mole of dicarboxylic 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, and then curing 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 cellulose paper stock a water-soluble cationic thermosetting resin formed by heating together at a temperature from about 110° C. to about 250° C. a C₆-C₉ saturated aliphatic diacid carboxylic acid and a polyalkylene polyamine in a mole ratio of polyalkylene polyamine to dicarboxylic acid of from about 0.8 to 1 to about 1.4 to 1, and then curing 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 C₆-C₉ saturated aliphatic diacid carboxylic acid with from about 0.8 to about 1.4 moles, per mole of dicarboxylic 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 said polyamide 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 C₆-C₉ saturated aliphatic diacid carboxylic acid with from about 0.8 to about 1.4 moles, per mole of dicarboxylic acid, of a polyalkylene polyamine at a temperature from about 45° C. to about 100° C. and in a ratio of epichlorohydrin to secondary amine groups of said polyamide from about 0.5 to 1 to about 1.8 to 1, and then curing the resin to a water-insoluble state.

6. A process for the production of wet-strength paper comprising sheeted cellulose 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 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
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 C₅₋₉ 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 C₅₋₉ 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 about 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 C₅₋₉ saturated aliphatic 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.

9. A process in accordance with claim 5 in which the dibasic carboxylic acid is a C₄₋₆ saturated aliphatic dibasic carboxylic acid.

10. A paper product in accordance with claim 8 in which the dibasic carboxylic acid is a C₄₋₆ saturated aliphatic dibasic carboxylic acid.

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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
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