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WET STRENGTH PAPER AND PROCESS FOR THE PRODUCTION THEREOF

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1

This invention relates to the manufacture of resin-treated cellulosic fibers and fibrous materials prepared therefrom, and is directed particularly to a method for improving the wet strength of felted fibrous cellulosic materials such as paper, board, 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 materials such as paper pulp.

It has been known for some time that the wet tensile strength and the bursting strength of paper can be increased by soaking the formed paper in strong solutions of urea-formaldehyde resin, followed by heating the paper to evaporate the water and cure the resin. In some paper mills the urea-formaldehyde resin solution has been applied by spraying the solution onto a moving web of paper, followed by passing the paper over or between heated drying rolls. However, a number of practical objections have developed to this method of treatment, the most serious of which is that the evaporation of the additional water introduced with the resin requires a second heating of the paper if it has first been dried, or, if the paper is impregnated while it is still wet, a material reduction in the speed of the drying drums. Despite these objections, however, the so-called "tub" treatment of preformed paper with concentrated aqueous solutions of synthetic resins is still used in some paper mills for special purposes, and the thermosetting resins hereinafter described may be applied by this method within the broader scope of the present invention if desired.

In order to avoid the difficulties inherent in tub treatment, more recent practice in most paper mills manufacturing wet strength paper has been to apply a melamine-aldehyde resin of a special type, known as colloidal cationic melamine-aldehyde resin. The discovery that this type of resin possesses substantive properties for hydrated paper stock, and can be applied to dilute paper pulp suspensions in small quantities with a high degree of retention and excellent wet strength in the finished paper, was made jointly with Charles S. Maxwell by one of the present applicants. The details of this method of producing wet strength paper are described in an article in the August 9,

2

1945 issue of the Paper Trade Journal. Briefly, melamine-formaldehyde resin is dissolved in a water solution of hydrochloric acid or another strong acid other than sulfuric acid to form a solution containing about 0.8 mol of acid for each mol of melamine and the solution is aged, whereby polymerization takes place and a blue haze develops, indicating the presence of resin particles in the colloidal range. This colloidal solution is added to the water suspension of hydrated paper stock in the beater, stock chest, Jordan engine, head box or at any other suitable point ahead of the papermaking wire or screen. The stock is then formed into paper by the usual procedure and carried over steam-heated drying rolls which dry the paper and cure the resin to a water-insoluble condition.

It is a principal object of the present invention to provide papermaking fibers and paper impregnated with a thermosetting resin having the properties of imparting wet strength thereto, and also imparting increased dry strength, which resin can be prepared and added to the slush stock in a paper mill in a slightly acid, neutral or alkaline condition. A further object is the provision of a resin of this character having a decreased sensitivity to the presence of large amounts of sulfate ion in the water containing the cellulose fibers. A still further important object is the provision of a thermosetting resin that can be cured under alkaline conditions, and which can therefore be readily used in the resin sizing of alkaline papers such as those containing calcium carbonate sizes and fillers. Still further objects will become apparent from the following descriptions of preferred embodiments of the invention.

We have found that the above and other objects are accomplished by applying to fibrous cellulosic material such as paper pulp or preformed and dried or partially dried paper an uncured thermosetting resin obtainable by condensing an alkylene polyamine with a halohydrin, as will hereinafter be more fully described. The resins of this class possess the property of imparting wet strength to paper when applied thereto in amounts on the order of 0.1% to 5% or more, based on the dry weight of the paper. We have also found, as one of the most important features of our invention, that the uncured thermosetting resins of the above class are substan-

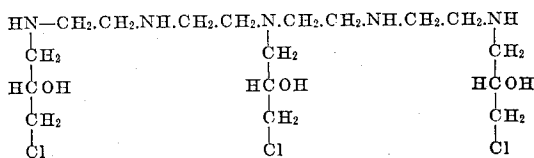
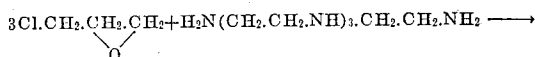
3

tive to fibers of hydrated cellulosic material such as paper pulp in aqueous solution; i. e. the resin is selectively adsorbed or absorbed by the cellulose fibers from a dilute aqueous solution or dispersion thereof containing these fibers in amounts much greater than those corresponding to the concentration of resin in the solution or to what would be contained in the water normally left in the sheet after forming. The importance of this discovery is evident, for it permits the application to cellulosic fibers of sufficient quantities of the resin to impart wet strength while the fibers are in dilute aqueous suspensions of the consistency used in paper mills, which is about 0.1% to 1% or, in pulp molding processes, at higher consistencies up to 2-2.5%.

The alkylene-polyamines used in preparing the resins employed in practicing our invention are well-known compounds corresponding to the formula $H_2N(C_nH_{2n}HN)_xH$ in which x is one or more. Typical amines of this class are the alkylene-diamines such as ethylenediamine and 1,3-propylenediamine and polyalkylene-polyamines such as diethylenetriamine, triethylenetetramine, tetraethylenepentamine and the corresponding polypropylene-polyamines and polybutylene-polyamines. The halohydrins are derivatives of glycerol in which one terminal hydroxy group is substituted by a halogen atom; i. e., by chlorine, fluorine, bromine or iodine, representative compounds being alphas-dichlorhydrin, epichlorhydrin and the like. We have found that the presence of a terminal halogen atom in these reagents imparts cationic properties to the resins which they form by reaction with alkylene-polyamines, and this is probably the reason why these resins are substantive to hydrated cellulose fibers.

In order to obtain a condensation product capable of cross-polymerization to form a resin a halohydrin should be used having at least two groups or radicals capable of promoting combination with an alkylene-polyamine. Such a compound is called by resin chemists a bi-functional or poly-functional halohydrin. The second combining radical may be another halogen atom, as in the dichlorhydrins or dibromhydrins or it may be an epoxide ring as in epichlorhydrin, or any other atom or group that is reactive to a polyamine. This type of poly-functional halohydrin is believed to react with a polyamine in two stages, the first being a simple linear condensation and the second a polymerization or self-alkylation reaction. The condensation between tetraethylenepentamine and epichlorhydrin is typical, and is believed to be as follows:

First stage

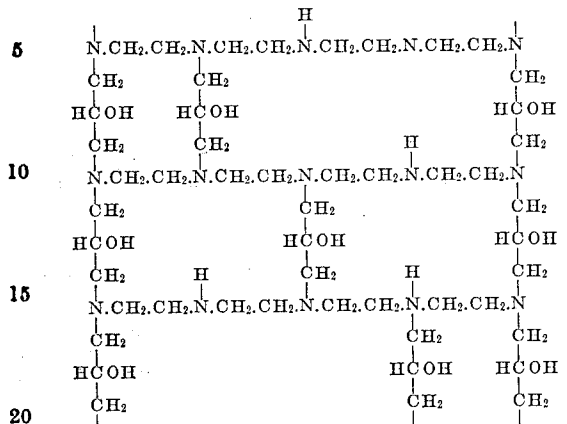


Second stage

Self-alkylation occurs between the chloro groups and the amine groups bearing hydrogen to form a three-dimensional or cross-linked molecule, thereby forming a thermosetting resin.

4

The structure of a representative portion of this molecule is as follows:



It is evident, therefore, that the essential reagents for preparing the thermosetting resins used in practicing the invention are (1) an alkylene-polyamine and (2) a poly-functional halohydrin such as a dihalohydrin, e. g. alpha-dichlorhydrin, dibromhydrin or di-iodhydrin or any of the corresponding monohalohydrins containing a second radical or group capable of reacting or promoting reaction with an alkylene-polyamine such as epichlorhydrin, epibromhydrin, epi-iodhydrin, di-epi-iodhydrin and the like.

The above reaction mechanism also suggests that more than one molecular proportion of the polyfunctional halohydrin should be present for each mol of tetraethylenepentamine if a thermosetting resin is to be obtained, and this has proven to be the case. When equimolecular quantities of epichlorhydrin and tetraethylenepentamine were reacted the product was not thermosetting and did not impart wet strength to paper; however the condensation product of two mols of epichlorhydrin or dichlorhydrin with one mol of the tetraethylenepentamine was thermosetting in character and produced paper of good wet strength. Further tests have shown that this ratio can be lowered to about 1.5:1 while obtaining thermosetting and wet strength-imparting properties, but for most practical purposes the 2:1 molar ratio marks the lower limit of the range wherein a commercially satisfactory wet strength resin is obtained. Larger proportions can be and usually are employed to increase the speed of cure of the resin, the optimum being between about 2:1 and 3:1. When more than 4 mols of the poly-functional halohydrin are used for each mol of tetraethylenepentamine the resin is thermosetting and produces wet strength paper, but the syrups are less stable in character and must be manufactured and stored at higher dilutions to avoid premature gelation.

It will readily be understood by those skilled in the art of synthetic resin manufacture that polyamines containing a smaller number of amino groups than tetraethylenepentamine will form thermosetting resins with correspondingly reduced molar proportions of poly-functional halohydrins; thus, as shown in Example 7, good results are obtained when the ratio of epichlorhydrin to diamines or triamines is 2:1.

The thermosetting resins applied to paper or paper stock by the present invention are therefore prepared by reacting one mol of an alkylene-

polyamine with at least 1.5 mols and preferably 2 or more mols of a polyfunctional halohydrin. This reaction is preferably carried out at temperatures below the boiling point of the mixture, usually not substantially higher than 60°-70° C., in order to permit the use of relatively concentrated solutions while obtaining the resin in a hydrophilic or water-dilutable condition. Usually the halohydrin is added slowly to the alkyl-
 enepolyamine, which is preferably dissolved in water or a water-miscible solvent such as aqueous ethanol, at a rate such that the reaction temperature is maintained at about 50°-55° C. The reaction product may then be maintained at 60°-70° C. until an increase in viscosity is noted, indicating that the second stage of the above-described reaction has set in, after which it is cooled and diluted with water if necessary to form a stable syrup. In some cases, and particularly where a dihalohydrin is being used, sufficient alkali such as sodium hydroxide, carbonate or phosphate should be added before or during the second stage of the reaction to neutralize the syrup by combining with any hydrohalide that is not taken up by the polyamine. This alkali addition also gives improved results when condensing a polyamine of relatively low molecular weight, such as ethylenediamine, diethylenetriamine or triethylenetetramine with several molecular proportions of a monohalohydrin such as epichlorhydrin. If desired the syrup may be subjected to a vacuum distillation after the first stage of the reaction is completed to remove any unreacted epichlorhydrin, dichlorhydrin or other poly-functional halohydrin.

As has been stated, the alkylenepolyamine-halohydrin resin solutions can be applied to paper or other felted cellulosic products by tub application methods if desired. Thus, for example, preformed and completely or partially dried paper prepared from kraft, sulfite or rag, soda, sulfate or ground wood stock or any mixture thereof may be immersed in a 3-10% aqueous solution of the resin and impregnated with about 90-100% thereof, based on the weight of the paper. The paper is then heated for about 1-4 minutes at temperatures of 212°-300° F. or higher, or for shorter times at higher temperatures, whereby the paper is dried and the resin is cured 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, cigarette paper and the like as well as heavier stock such as wrapping paper, bag paper and the like to impart wet strength characteristics thereto.

The preferred process of the present invention, however, takes advantage of the substantive properties of the halohydrin-alkylenepolyamine resins for hydrated cellulosic fibers. In practicing this process the resin in its uncured and hydrophilic or water-dilutable condition is added to an aqueous suspension of the paper stock, such as any of those enumerated above, in the beater, stock chest, Jordan engine, head box or at any other suitable point ahead of the papermaking wire or screen followed by forming the treated fibers into a felted product on the wire or cylinder. The felted product is then heated in the usual manner to dry the paper or board, thereby curing the resin to its polymerized and water-insoluble condition and imparting wet strength to the paper.

As is noted above, the thermosetting reaction products of alkylenepolyamines with poly-func-

tional halohydrins impart substantial wet strength to paper and other products formed of felted cellulosic fibers when present therein in amounts of about 0.5-5% or more. The quantity of resin to be added to the aqueous stock suspension will depend on the degree of dry and wet strength desired in the finished product and on the per cent of resin retained by the paper fibers. Thus, for example, with a 50% resin retention in the stock, 6% of resin should be added to produce a wet strength paper containing 3% of resin, based on the dry weight of the paper. The resin remaining in the white water can be re-used in treating further quantities of paper by employing a closed or partially closed or recirculating white water system; i. e., by using a part or all of the white water from the papermaking machine for preparing further batches of paper pulp suspension.

We have found that the uncured alkylenepolyamine-halohydrin resin contained in paper, whether introduced as a tub size or combined with the cellulosic fibers prior to sheet formation by adsorption in aqueous suspension, can be cured under acid, neutral or alkaline conditions by subjecting the paper to a heat treatment. This is of considerable importance, since it permits addition of the water-soluble resin to the paper stock suspension in the beater or stock chest of a paper mill along with clay, alum, resin size, talc, calcium carbonate and other suitable sizing or loading materials. Even when large quantities of calcium carbonate are added, which cause the paper to be alkaline in character, the resin can be cured by heating between steam-heated rolls in the usual manner at temperatures of 212°-350° F. or higher. The resin can also be used successfully with acidic materials; thus, for example, it has been applied to aqueous paper pulp in admixture with the melamine resin acid colloid described above and cured in the resulting paper without difficulty.

The invention will be illustrated in greater detail by the following specific examples. It should be understood, however, that although these examples may describe in detail some of the more specific features of the invention they are given primarily for purposes of illustration and the invention in its broader aspects is not limited thereto.

EXAMPLE 1

A solution of 37.8 grams (0.2 mol) of tetraethylenepentamine in 93 grams of water was prepared and epichlorhydrin was added with stirring at a rate such that the reaction temperature did not rise above 50° C. After 35.5 grams (0.6 mol) of epichlorhydrin had been added the stirring was continued at 50° C. until the product had become viscous. The resulting hydrophilic colloid was diluted with water to a 15% solution.

Bleached kraft paper pulp was suspended in water and refined 2 minutes, diluted with water to a fiber consistency of 0.6%, and divided into a number of samples. The above-described epichlorhydrin-polyalkylenepolyamine resin was added to all of these samples except one control. The pH of the resin-treated fiber suspensions was then adjusted to the values shown in the following table by adding hydrochloric acid or sodium hydroxide or, in sample No. 8, by adding aluminum sulfate, and the samples were made into handsheets on a laboratory papermaking machine. All the sheets were heated one minute at 230° F. to dry the paper

7

and cure resin, and sheets from each sample were also given an additional cure of 10 minutes at 260° F. The sheets were then tested for wet and dry tensile strength.

In the following table the per cent resin added is based on the dry weight of the kraft fibers; the per cent retained is based on the amount of resin added, and the basis weight is the weight in pounds of 500 sheets 24 inches by 40 inches in size. The tensile strength was measured on 4 x 0.5-inch strips, but is reported as pounds per inch width.

Sample No.	pH of Stock	Per Cent Resin		Basis Weight	Tensile Strength, lbs./inch			
		Added	Retained		Dry	Wet	Dry ¹	Wet ¹
1	4.0	1.5	42	49.0	23.2	2.6	24.0	5.2
2	4.5	1.5	49	48.7	21.0	3.0	21.4	5.0
3	6.0	1.5	53	48.4	23.0	3.2	24.0	5.6
4	8.0	1.5	67	48.4	25.0	4.2	24.4	6.4
5	10.0	1.5	67	49.9	24.2	4.6	24.0	6.0
6	8.0	3.0	35	49.5	22.6	4.4	23.2	6.4
7	4.5	3.0	31	48.7	21.4	3.4	22.4	5.2
8	Alum	3.0	24	50.4	22.0	4.0	22.8	6.2
	4.5							
9	4.5	6.0	12	50.1	22.0	3.4	22.8	5.8
10	4.5	None		50.0	19.4	0.4	18.4	0.6

¹ After additional heating.

These results show that good wet strength is obtained under both acid and alkaline conditions with the thermosetting epichlorhydrin-polyalkylenepolyamine resin. However, the retention and wet strength are better under alkaline conditions.

EXAMPLE 2

The folding endurance of paper prepared from stock suspensions pretreated with thermosetting epichlorhydrin-polyalkylenepolyamine resin is greatly increased over that of paper made from the same stock which contains no resin. This is shown in the following table, the paper being made from samples of the resin-treated stock described in Example 1 by the procedure described in that example.

Sample No.	pH of Stock	Per cent Resin		Basis Weight	Tensile Strength		MIT Fold	Tensile ¹ Strength	
		Added	Retained		Dry	Wet		Dry	Wet
1	4.5	3.0	38	47.8	24.4	3.0	557	24.8	5.8
2	8.0	3.0	43	48.9	25.2	4.4	624	25.4	6.6
3	4.5	1.5	53	48.2	24.2	2.8	604	25.4	6.4
4	4.5	0.75	76	49.2	23.6	2.4	718	24.0	4.6
5	Alum	0.75	57	47.9	23.2	2.0	636	24.6	4.4
	4.5								
6	4.5	None		48.7	22.0	0.6	388	21.8	0.6

¹ After an additional 10-minute cure at 260° F.

These figures also show that paper having good wet strength is obtained when even small quantities of the resin are used.

EXAMPLE 3

Following the procedure described in Example 1 a series of resin syrups was made from tetraethylenepentamine with varying molar ratios of epichlorhydrin and tested by adding 3% of the resin to an 0.6% water suspension of bleached kraft paper pulp, followed by forming the treated stock into handsheets, heating one minute at 230° F., and testing for dry and wet tensile strength and folding endurance. The results are given in the following table in which the heading "Ratio" means the molar ratio of epichlorhydrin

8

to tetraethylenepentamine and the tensile strength is in pounds per inch width.

Sample No.	Ratio	Tensile Strength		MIT Fold
		Dry	Wet	
1	1:1	22.6	0.4	466
2	1.5:1	25.2	1.8	598
3	2:1	23.8	3.4	626
4	2.5:1	23.8	3.4	602

EXAMPLE 4

Bleached kraft paper pulp was dispersed in water in a laboratory beater, beaten to hydrate the stock, refined 2 minutes in a Morden refiner and diluted to 0.6% fiber consistency. Three per cent of the epichlorhydrin-polyalkylenepolyamine resin of Example 1 was added followed by 100% of calcium carbonate filler, based on the dry weight of the paper fibers. The stock was then made into handsheets, some of which were given a second cure of 10 minutes at 260° F. in addition to the regular heating for one minute at 230° F. The sheets were tested for resin content

and for dry and wet tensile strength in the usual manner, with the following results:

Sample No.	Per Cent Resin Added	Per Cent Resin Retained	Basis Weight	Tensile Strength			
				Dry	Wet	Dry ¹	Wet ¹
1	None		49.7	9.6	0.4	10.4	<0.4
2	3	37	43.2	11.4	2.4	12.4	3.2

¹ After additional heating.

EXAMPLE 5

Another advantage of the thermosetting polyalkylenepolyamine resins is the fact that they will function well in water containing large quantities of dissolved salts. In order to demonstrate

9

this property, both the stock and recirculated white water were adjusted by the addition of sodium sulfate to give the desired sulfate ion concentration and 3% of resin, based on the dry weight of the stock, was added and handsheets were made and tested with the following results:

Sample No.	SO ₄ p. p. m.	Per Cent Resin Retained	Basis Weight	Tensile Strength			
				Dry	Wet	Dry ¹	Wet ¹
1.....	None	28	49.9	22.0	2.4	22.6	4.4
2.....	500	54	49.6	23.0	4.0	24.8	7.2
3.....	1,000	52	49.2	23.6	4.0	25.0	7.0
4.....	1,500	45	50.1	23.4	3.8	24.8	6.6
5.....	2,500	42	48.9	22.8	3.8	24.6	6.8

¹ After additional 10-minute cure at 260° F.

EXAMPLE 6

A solution of 94.5 grams (0.5 mols) of tetraethylenepentamine in 492 grams of water was prepared and 161.2 grams (1.25 mols) of dichlorhydrin (ClCH₂.CH(OH).CH₂Cl) was added slowly with agitation while maintaining the temperature below 20° C. The syrup was then cooled to 10° C. and a solution of 51.5 grams of 97% NaOH in 150 grams of water was added. The mixture was agitated for 3 hours to initiate the formation of a thermosetting resin. The resulting resin syrup, having a pH of 8.0 and a solids content of 22%, was diluted with water to 10% solids and was stable for several weeks at this concentration.

The resin was added to aqueous 0.6% suspensions of bleached kraft paper pulp, using 3% of resin on the dry weight of the pulp, with and without the addition of aluminum sulfate. Handsheets were made from the treated stock and tested for dry and wet tensile strength in the usual manner. The sheets containing the resin with no alum had dry and wet strengths of 26.0 and 4.8 pounds per inch width, respectively. The corresponding figures for sheets containing 3% alum along with the resin were 28.2 and 5.8 pounds.

EXAMPLE 7

Resin No. 1

To a solution of 25.75 grams of diethylenetriamine in 83.7 grams of water there was added slowly 57.9 grams of epichlorhydrin while maintaining the temperature at 50° C. When the initial condensation was complete 11.3 grams of trisodium phosphate was added and the solution was heated at 200° F. until an increase in viscosity indicated that the second stage of the condensation had been reached. This required about one hour. The resulting resin syrup was diluted with water to about 10% solids.

Resin No. 2

A solution of 30 grams of ethylenediamine in 109 grams of water was prepared and 92.5 grams of epichlorhydrin was added slowly while cooling the mixture to 50° C. After this addition the solution was heated to about 70° C., 18 grams of trisodium phosphate was added, and heating was continued to form a resin syrup which was cooled and diluted.

Resin No. 3

To a solution of 36.5 grams of triethylenetetramine in 92 grams of water there was slowly added 55.5 grams of epichlorhydrin at 50° C. The resulting syrup was further reacted by heating to an increased viscosity and diluted to 10% solids.

10

Each of these resin syrups was added to an 0.6% suspension of kraft paper pulp in water, using 3% of the resin based on the dry weight of the pulp, and the treated stock was made into handsheets which were cured at 230° F. for one minute. Some of the sheets from each batch were given an additional cure of 10 minutes at 260° F. The sheets were then tested for dry and wet tensile strength and folding endurance. In the following table the tensile strengths are given in pounds per inch width of the paper.

Resin No.	Tensile Strength		After 10 min. Cure Tensile Strength		MIT Fold
	Dry	Wet	Dry	Wet	
1.....	24.2	4.2	25.2	6.4	721
2.....	24.0	2.8	25.2	5.0	619
3.....	23.2	1.4	23.4	3.0	551

What we claim is:

1. Paper having a uniform content of about 0.5-5% of its dry weight of a cured thermosetting alkylenepolyamine-polyfunctional halohydrin resin.

2. Paper having a uniform content of about 0.5-5% of its dry weight of a cured thermosetting resin, said resin being the condensation product of one molecular proportion of an alkylenepolyamine with at least 1.5 mols of a polyfunctional halohydrin.

3. Paper having a uniform content of about 0.5-5% of its dry weight of a cured thermosetting tetraethylenepentamine-polyfunctional halohydrin resin.

4. Paper impregnated uniformly with the heat-cured condensation product of one mol of a polyalkylenepolyamine with at least two mols of a dihalohydrin.

5. Paper impregnated uniformly with the heat-cured condensation product of one mol of a polyalkylenepolyamine with at least two mols of an epihalohydrin.

6. Paper impregnated uniformly with the heat-cured condensation product of one mol of an ethylenepolyamine with at least two mols of an alphasdihalohydrin.

7. Paper impregnated uniformly with the heat-cured condensation product of one mol of an ethylenepolyamine with at least two mols of an epihalohydrin.

8. Paper impregnated uniformly with the heat-cured condensation product of one mol of a polyethylenepolyamine with at least two mols of alphasdichlorhydrin.

9. Paper impregnated uniformly with the heat-cured condensation product of one mol of a polyethylenepolyamine with at least two mols of epichlorhydrin.

10. Paper carrying an alkaline filler and having a uniform content of a cured thermosetting alkylenepolyamine-polyfunctional halohydrin, the amount of said resin being about 0.5-5% based on the dry weight of said paper exclusive of the weight of said filler.

11. Paper according to claim 10 in which the filler is calcium carbonate.

12. A process for the production of cellulosic products of increased wet strength which comprises adding to an aqueous suspension of cellulosic paper stock an uncured thermosetting alkylenepolyamine-polyfunctional halohydrin resin, adsorbing about 0.1% to 5% of said resin on said paper stock, forming the stock so treated into a waterlaid cellulosic product, and

11

curing the resin to its heat-set and water-insoluble condition by heating said waterlaid product for about 1 to 4 minutes at temperatures between 300° and 212° F. and thereby forming a bond of cured resin between the cellulosic fibers thereof. 5

13. A process according to claim 12 in which the resin is a polyethylenepolyamine-epichlorhydrin resin.

14. A process for the production of wet strength paper which comprises adding to an aqueous suspension of cellulosic paper stock an uncured thermosetting alkylenepolyamine-polyfunctional halohydrin resin, adsorbing about 0.1% to 5% of said resin on said paper stock, forming the stock so treated into a waterlaid sheet, and curing said resin to its heat-set and water-insoluble condition by heating said sheet for about 1 to 4 minutes at temperatures between 300° and 212° F. and thereby forming a bond of cured resin between the cellulosic fibers thereof. 10

15. A process according to claim 14 in which the resin is a polyethylenepolyamine-epichlorhydrin resin. 15

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