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(54) **Title:** WET STRENGTH RESIN COMPOSITION AND METHOD OF MAKING SAME

(57) **Abstract**

A composition is comprised of an aminopolyamide-epichlorohydrin acid salt resin having a total organically bound clorine of up to 0.7 % by weight of the resin is useful as a wet strength agent for paper. The composition further comprised of a polyol, a monoalkyl ether of a polyol, and/or a polyalkylene glycol is useful as an additive in coating formulations. The amount of total organically bound chlorine present is controlled by the manufacturing process parameters.

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WET STRENGTH RESIN COMPOSITION AND METHOD OF MAKING SAME

CROSS-REFERENCE TO RELATED APPLICATIONS

This is a continuation-in-part application of application serial number 07/740,369, filed on August 5, 1991, the entire contents of which are incorporated herein by reference, which is a continuation-in-part of application serial number 07/712,327, filed on June 7, 1991 which is a continuation-in-part of application serial number 07/652,346, filed on February 7, 1991 which is a continuation-in-part of application serial number 07/573,600, filed on August 24, 1990.

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to wet strength resin compositions for paper and coating applications and a method for making them.

2. Description of the Related Art

Aminopolyamide-epichlorohydrin resins were the first commercially significant neutral-to-alkaline curing wet strength resins for paper. In addition to the health and safety benefits that result from the resins being formaldehyde-free, their use also affords such benefits as

reduced paper-machine corrosion and improved softness and absorbency in treated webs compared to urea-formaldehyde-treated webs.

One of the drawbacks associated with the use of aminopolyamide-epichlorohydrin wet strength resins is the emission of harmful chlorinated compounds into the water systems of pulp and paper mills. These chlorinated compounds, which are the by-products of the manufacture of the aminopolyamide-epichlorohydrin resins, have been identified as epichlorohydrin, 1,3-dichloro-2-propanol, and 3-chloro-1,2-propanediol. These chlorinated organics are usually discharged into effluent waste water systems from pulp and paper mills because they are only partially substantive to cellulose pulp fibers. Since permissible amounts of halogenated organics in waste waters is ever decreasing, considerable effort has been expended to reduce the amount of these materials in aminopolyamide-epichlorohydrin wet strength resins.

The wet strength resin compositions according to the invention contain organic chlorine compounds in amounts which are at least 99% lower than commercial aminopolyamide-epichlorohydrin resins.

The related art does not teach wet strength resins compositions comprised of an aminopolyamide-epichlorohydrin acid salt resin and up to 0.7% by weight total organically bound chlorine based on the weight of said resin. The related art also does not teach a relationship between the temperature at which alcohol is removed in the aminopolyamide resin-making process and the wet strengthening ability of the aminopolyamide-epichlorohydrin resin made from the aminopolyamide resin. The related art also does not teach a relationship between the epichlorohydrin-aminopolyamide reaction time and very low total organically bound chlorine content in processes to make wet strength resins compositions comprised of an aminopolyamide-epichlorohydrin acid salt resins.

SUMMARY OF THE INVENTION

The present invention provides a wet strength resin composition comprising water, and from about 1% to about 60% by weight of an aminopolyamide-epichlorohydrin acid salt resin, up to 0.7% by weight total organically bound chlorine based on the weight of said resin.

The wet strength resin compositions according to the invention can be made by a process whose first step is the aminolysis of an ester. A C_{1-3} dialkyl ester of a saturated aliphatic dicarboxylic acid having from 3 to 6 carbon atoms is heated with a polyalkylenepolyamine having two primary amine groups and at least one secondary amine group in the absence of water. The ester to polyalkylenepolyamine molar ratio has a value of up to 1:1. During the heating step, the reaction temperature first reaches a maximum of about 150°C-160°C at which point the alcohol formed as a result of the reaction between the diester and the polyalkylenepolyamine begins to boil. The alcohol is retained in the reaction by refluxing it which also lowers the reaction temperature. After the temperature drops to about 110°C-115°C, the alcohol is removed from the reaction at a temperature of from about 110°C to about 160°C. The alcohol removal is continued until the viscosity of a 50% aqueous solution of resulting polyamidopolyamine at 25°C reaches at least 700 cps. At this point, epichlorohydrin is added to an aqueous solution of the polyalkylenepolyamine at such a rate that the reaction temperature is maintained in the range of from about 5°C to about 30°C. After all the epichlorohydrin has been added, the resulting reaction mixture has an E/N ratio of from 0.6 to 1.08. Then the temperature of the reaction mixture is maintained in a range of from about 15°C to about 35°C until all of the epichlorohydrin has reacted as indicated by analysis of the reaction mixture. The pH of the reaction mixture is then adjusted to a value of up to about 7.0. The process produces a wet strength resin composition comprised of an aqueous solution of an aminopolyamide-

epichlorohydrin acid salt resin which has a total organically bound chlorine of up to 0.7% by weight of said resin. The wet strength resin compositions according to the invention can also be modified for use in coating formulations. Such modified compositions contain one or more solvents as disclosed herein in addition to the aminopolyamide-epichlorohydrin acid salt resin.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Other than in the operating examples, or where otherwise indicated, all numbers expressing quantities of ingredients or reaction conditions used herein are to be understood as modified in all instances by the term "about".

Polyalkylenepolyamines which can be used according to the invention are those which have two primary amine groups and at least one secondary amine group such as diethylenetriamine, triethylenetetramine, tetraethylenepentamine, and bis-hexamethylenetriamine and the like. The dicarboxylic acid esters which can be used in the process according to the invention are those which are C_{1-3} diesters of C_{3-6} dicarboxylic acids. Such diesters can be made for example, by direct esterification of a dicarboxylic acid having from 3 to 6 carbon atoms with an alcohol having from 1 to 3 carbon atoms. Examples of such esters include but are not limited to dimethyl malonate, dimethyl succinate, dimethyl adipate, and dimethyl glutarate. Mixtures of any or all of such esters can also be used in the process according to the invention. Preferably, the esters are mixtures of dimethyl adipate and dimethyl glutarate which are sold as DBE-2™, a product of the DuPont Corporation.

The molar ratio of ester to polyalkylenepolyamine in the aminolysis step should not exceed 1:1. Values greater than 1:1 will result in gelation of the reaction product. Preferably, the ester- polyalkylenepolyamine reaction mixture is heated at atmospheric pressure in a reaction vessel equipped with a reflux condenser until the

temperature first reaches a value of about 150°C-160°C during which time the alcohol formed in the reaction begins to reflux. The refluxing alcohol removes heat from the reaction mixture and the temperature continuously falls as more and more alcohol is produced. When the reaction temperature drops to about 110°C, the alcohol is removed at a temperature in the range of from about 110°C to about 160°C. The alcohol removal can be accomplished by changing the condenser configuration from reflux to take-off. Alcohol is continuously removed until the viscosity of a 50% aqueous solution of resulting polyamidopolyamine at 25°C reaches at least 700 cps. and preferably 1000 cps. If the alcohol removal is accomplished at a temperature lower than 110°C, the viscosity of a 50% aqueous solution of the polyamidopolyamine at 25°C will not reach at least 700 cps and the resulting wet strength resin will not increase the wet tensile of a treated sheet to an acceptable level. Table II shows the effect of the viscosity of a 50% aqueous solution of the polyamidopolyamine (PAA) resin on the wet tensile development of a treated sheet. The higher the viscosity of a 50% aqueous PAA solution the higher the wet tensile ratio and the more closely the particular low TOCl resin behaves like a commercial resin which is at least one order of magnitude higher in TOCl. Since it has been found that product gelation results if the molar ratio of ester to polyalkylenepolyamine exceeds 1:1, it is important to insure that substantially all of polyalkylenepolyamine reacts before the alcohol formed in the reaction is removed. Premature alcohol removal can result in the simultaneous removal of some of the polyalkylenepolyamine thereby altering the ester/polyalkylenepolyamine molar ratio sufficient to result in product gelation. Retention of the alcohol in the reaction mixture for example by refluxing, insures that no polyalkylenepolyamine is lost before it reacts with the ester.

The polyamidopolyamine formed in the aminolysis reaction is then reacted with epichlorohydrin in aqueous

solution to form an aminopolyamide-epichlorohydrin resin. The concentration of the aminopolyamide in the water is not critical as long as the combined reaction solids content of aminopolyamide and epichlorohydrin present after step (c) are in the range of from about 5% to about 60% by weight. The preferred % aminopolyamide solids in step (b) of the process is from about 29% to about 39% by weight. The relative amounts of aminopolyamide-epichlorohydrin resin are expressed as the E/N ratio. The E/N ratio is defined by Equation I as

$$\frac{\textit{moles epichlorohydrin}}{\textit{amine equivalents}} \quad \textit{Eq.I}$$

where the amine equivalents is defined by Equation II as

$$\frac{\textit{wt. of aminopolyamide sol'n x \% solids as decimal x TA}}{56110} \quad \textit{Eq.II}$$

and TA, which is total alkalinity, is defined by Equation III as

$$\frac{\textit{volume (ml) x normality of stnd. acid x 56.11}}{\textit{wt. of aminpolyamide sol'n x \% solids as decimal}} \quad \textit{Eq.III}$$

The total alkalinity of a typical aminopolyamide is in the range of from about 270 to about 380 mg/g of KOH on a solids basis. The amount of epichlorohydrin to be added in step (c) of the process is calculated by substituting the numerical value for the amine equivalents as calculated by Equation II into Equation I, setting the E/N value equal to about 0.9, and solving the equation for moles of epichlorohydrin. The epichlorohydrin is added to the aminopolyamide solution neat at a rate sufficient to maintain the temperature of the reaction mixture in the range of from about 5°C to about 30°C, preferably from about 10°C to about 15°C. In step (d) the temperature of

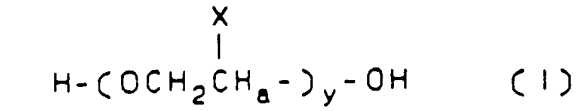
the reaction mixture is then maintained in a range of from about 15°C to about 35°C until all of the epichlorohydrin has reacted. The epichlorohydrin reaction time referred to in Table I is the time required for step (d) and can be determined by analysis of the reaction mixture for total organically bound chlorine as described in Example 19. All of the epichlorohydrin has reacted when the total organically bound chlorine is less than about 7000 ppm (0.7% by weight) based on reaction solids. The epichlorohydrin reaction time can also be determined from viscosity measurements of the reaction mixture by means of a Brookfield viscometer using a #2 spindle at 30 r.p.m. at 25°C. When step (d) of the process is carried out at a preferred total solids content of about 45%, the epichlorohydrin reaction temperature is maintained until the Brookfield viscosity of the reaction mixture falls within the range of from about 500 to about 1500 cps. In another preferred embodiment, when the total solids content of step (d) is 40%, the epichlorohydrin reaction temperature is maintained until the Brookfield viscosity of the reaction mixture falls within the range of from about 350 to about 800 cps. In yet another preferred embodiment, when the total solids content of step (d) is 35%, the epichlorohydrin reaction temperature is maintained until the Brookfield viscosity of the reaction mixture falls within the range of from about 200 to about 500 cps. The product formed in step (d) is an epichlorohydrin-aminopolyamide resin. After the temperature has been held in the range disclosed above, the reaction is stopped by adjusting the pH of the reaction mixture to a value of less than about 7. The addition of an amount of water to reach a desired final % solids level followed by pH adjustment can also stop the reaction. The preferred final solids content is from about 35% to about 45% by weight of solution. The pH of the reaction mixture is always adjusted by acidification regardless of whether water is or is not added to stop the reaction. The acidification can

be accomplished by any means known to those of ordinary skill in the art. For example, a gaseous acid such as anhydrous hydrogen chloride can be introduced into the aqueous reaction mixture or an aqueous acid solution can be added. Preferably an aqueous acid solution is used to adjust the pH to a value of less than about 7.0 such as hydrochloric acid, sulfuric acid, phosphoric acid, acetic acid, propionic acid, or benzoic acid. The preferred aqueous acid solution is hydrochloric acid. While any pH value of less than about 7.0 can be achieved, the preferred value is in the range of from about 2 to about 4. The process according to the invention produces a wet strength resin composition comprising an aminopolyamide-epichlorohydrin acid salt resin and a total organically bound chlorine of less than 0.7% by weight of the aminopolyamide-epichlorohydrin acid salt resin. The total organically bound chlorine is determined by the method described in Example 19.

The process according to the invention produces unexpectedly low levels of total organically bound chlorine in a wet strength resin which performs at least as well as resins which have one to two orders of magnitude more total organically bound chlorine because during the synthesis of the aminopolyamide the aminolysis of the esters is carried out until the viscosity of a 50% aqueous solution of resulting polyamidopolyamine at 25°C reaches at least 700 cps and the epichlorohydrin reaction is carried out at relatively low temperatures and at the relatively low E/N ratio from 0.6 to 1.08. A resin prepared by the process according to the invention but having an E/N ratio of greater than 1.08 will have an unacceptably high TOCl content when used as an additive in the manufacture of paper such as wet strength resin applications, retention aids, and the like. An unacceptably high TOCl content for such applications, is one which is greater than 0.7% by weight of the aminopolyamide-epichlorohydrin acid salt resin. However, when the compositions according to the

invention are used in coatings applications, the E/N ratio can have a value as great as 2.0. Such a value of the E/N ratio will cause the TOCl content of the resin to be greater than 0.7%. based on total resin weight. Examples 2-11 are resins prepared by the process according to the invention which produces the combined effects of low total organically bound chlorine and wet tensile development equal to resins containing up to about 2 orders of magnitude more total organically bound chlorine. Examples 12-17 are resins prepared by the methods according to the prior art and show the effects of elevated epichlorohydrin reaction temperatures at equal or greater E/N ratios for resins prepared according to the process of the invention. Conventional wisdom dictates that optimum wet strength performance and minimum total organically bound chlorine levels are favored by optimizing the epichlorohydrin reaction which is in turn favored by reaction temperatures greater than room temperature and E/N ratios of from 0.6 to 1.08.

When the compositions according to the invention are used in coatings applications, the compositions will contain one or more water-miscible solvents selected from the group consisting of: (a) a monoalkyl ether of a polyol such as methyl carbitol(diethylene glycol monomethyl ether, butyl carbitol (diethylene glycol monobutyl ether, and the like); (b) a polyol which is any aliphatic compound having 2 or more hydroxyl functionalities that is miscible with water or combinations thereof. Examples of such polyols include but are not limited to ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, diethylene glycol, dipropylene glycol, triethylene glycol, 1,6-hexylene glycol, glycerol, monosaccharides such as glucose or fructose, disaccharides such as sucrose, and polyvinyl alcohol. Also included in this group are compounds of the formula I



$$H\text{-}(OCH_2CH_a\text{-})_y\text{-}OH \qquad (I)$$

wherein X is H, CH_3, C_2H_5; a is 1 or 2; and y is less than 10. The preferred solvents are 1,2-propylene glycol, methyl carbitol, polyethylene glycol 200 (PEG 200), and a mixture comprised of 10% by weight of 1,6-hexanediol and 90% by weight of butyl carbitol.

When the compositions according to the invention contain one or more solvents as disclosed herein, they can be used for coatings applications such as components in ink formulations or as epoxy resin curing agents. When the compositions according to the invention are used in coatings applications, they will typically contain from 10 to 60% by weight of aminopolyamide-epichlorohydrin acid salt resin, from 5% to 95% solvent, and from 0 to 85% water. The preferred values are 30-35% PAE resin, 20-35% solvent, and 30-50% water.

When the composition according to the invention are used in coatings applications, the solvent or solvents can be added during the manufacture of the aminopolyamide-epichlorohydrin acid salt resin before the addition of the epichlorohydrin or the solvent or solvents can be added after the resin manufacture is complete.

The present invention also provides cellulosic fibrous webs comprising a wet strengthening effective amount of an aminopolyamide-epichlorohydrin acid salt resin and less than 0.7% of total organically bound chlorine by weight of said aminopolyamide-epichlorohydrin acid salt resin. A wet strengthening effective amount of an aminopolyamide-epichlorohydrin acid salt resin is any amount required to reach a desired wet strength as determined by wet tensile measurements. Different applications will require different amounts of wet tensile and hence different amounts of wet strength resin composition containing an aminopolyamide-epichlorohydrin acid salt resin. The relationship between

the amount of wet strength resin composition added to a cellulosic fibrous web and the wet tensile produced therefrom is dependent upon a number of factors such as the nature of the pulp fibers and the method of application and is readily determinable by one of ordinary skill in the art. The wet strength resin compositions according to the invention are normally applied to cellulosic pulp fibers at dosage level of from about 1 to about 30 pounds of dry wet strength resin per ton of fiber to produce wet strengthened webs. The wet strength resin compositions according to the invention can be applied to cellulosic pulp fibers by any method known to those of ordinary skill in the art such as by spraying, dipping or coating a pre-formed sheet or in the wet end of a paper machine since the aminopolyamide-epichlorohydrin acid salt resins in the wet strength resin compositions are substantive to cellulose pulp fibers. The preferred amount of dry wet strength resin per ton of fiber is in the range of from about 4 to about 12 lbs pounds per ton. The following examples will serve to illustrate but not limit the invention.

Example 1

Preparation of an Aminopolyamide Resin

To a resin reactor was charged one mole of a dibasic acid ester mixture comprised of 65% dimethyl glutarate and 35% dimethyl adipate and one mole of diethylene triamine. Stirring and nitrogen sparge were started and the contents of the reactor were heated to 150°C-160°C. Methanol began to reflux at about 157°C. The reflux was allowed to continue until the reaction temperature reached 125°C at which time the methanol was distilled off. The reaction temperature was maintained in the 140°C-160°C range during the approx. 3 hours required for distillation of about 85% of the theoretical amount of methanol. The Brookfield viscosity (spindle #3 @ 12 rpm) of a 48.4% aqueous solution of the resin thus obtained was 2850 cps. A 33.5% solids resin solution had a total alkalinity of 376 mg KOH/g on a solids basis and a Brookfield viscosity (spindle #2 @ 60

rpm) of 280 cps.

Examples 2-17

Examples 2-11 describe the preparation of wet strength resin compositions according to the invention and prepared according to the process of according to the invention. Examples 12-17 describe the preparation of resin compositions using reaction parameters outside the scope of the process according to the invention. The entries in Table I list the various reaction parameters, wet strength performance, and total organically bound chlorine of compositions corresponding to examples 2-17. Examples 3-11 were prepared exactly like the procedure of Example 2. Comparisons of resins in Examples 2-11 to those in Examples 12-17 should be made only for those resins having the same E/N values. For example, the properties of the resin of Example 5 should be compared with those of Example 13 because both resins have an E/N ratio equal to 0.7.

Example 2

Preparation of Wet Strength Resins Compositions

To a round bottom flask were charged 171 grams of a 48.0% solids aminopolyamide resin solution having a total alkalinity based on solids content (TA) of 274.8 mg KOH/g and 38 grams of water. Gentle stirring was applied and the contents of the flask were cooled to about 15°C (ECH addition temperature) at which time about 26 grams of epichlorohydrin were added over 3 hours. After completion of the epichlorohydrin addition, the contents of the reactor were allowed to exotherm to a temperature of about 20°C. The reaction mass was held at this temperature for 12.5 hours (ECH reaction temperature & time). The viscosity at this point (Final Visc.) was 602 cps. The reaction was stopped by adjusting the pH of the solution to 2.0 with 37% hydrochloric acid. The resin solution contained 45.6% solids and 0.044% total organic chlorides based on the resin solids (% total Cl) as determined by extraction-G.C. method. (Example 19)

Example 18

Performance Testing of Wet Strength Resin Compositions

1. Stock Preparation

Kraft softwood lapboard (Bowater) was beaten in a large capacity Waring Blender at 4.1% consistency for 10 minutes at 15,500 r.p.m. and then further diluted to 0.27% consistency. The drainage of the diluted stock was measured at 110-120 ml by "30 Second Britt Drainage" method using a 4" circular 70 mesh screen with the Mark IV Dynamic Handsheet Mold/Paper Chemistry Jar Assembly.

2. Handsheet Preparation

Blank handsheets were prepared according to the handsheet preparation method outlined in the Mark IV Dynamic Handsheet Mold/Paper Chemistry Jar Assembly operating manual. Treated handsheets were prepared by the same method except a dosage of 8 dry pounds wet strength resin per ton of dry pulp was manually added to the dispersed stock slurry and the furnish was mixed at 750 r.p.m. for 55 seconds. Handsheets were blotted dry between felt sheets and pressed with a rolling pin in back and forth and diagonal directions. Pressed sheets were placed between drying rings and conditioned overnight at 50% humidity and 70°C as per instructions in the Mark IV Dynamic Handsheet Mold/Paper Chemistry Jar Assembly operating manual. The dosage level for all sheets used to generate the data given in Tables I and II was 8 lbs resin /ton pulp.

3. Wet Tensile Determination

Tensile strips measuring 1" by 4" were cut from treated handsheets and soaked for 1 hour in water at 25°C. Tensile strengths were determined on an Instron Tensile Tester using a 10 lb load cell. The wet tensile ratio, R, of Tables I and II is defined as the ratio of the wet tensile of a sheet treated with a wet strength resin composition according to the invention to the ratio of the wet tensile of commercial product B which is Fibrabond 33™, a product of Henkel Corporation, Ambler, PA. Product A in

Table I is Kymene 557H™, a product of Hercules, Wilmington, DE.

Table I

			ECH Addition		ECH Reaction				
Resin	E/N	% Rx Slds	T[1]	°C[2]	T[3]	°C[4]	Vis[5]	R[6]	%Cl
Ex. 2	0.7	45	3.0	15	12.5	20	602	0.9	0.04
Ex. 3	0.7	40	3.0	15	18.25	15	347	1.1	0.04
Ex. 4	0.7	40	1.0	10	14.0	20	375	0.9	0.05
Ex. 5	0.7	35	3.0	15	14.5	20	198	1.0	0.05
Ex. 6	0.7	45	3.0	10	11.75	20	640	0.9	0.03
Ex. 7	0.7	45	3.0	10	10.0	22.5	670	0.9	0.03
Ex. 8	0.7	45	1.0	10	7.5	25	660	1.0	0.04
Ex. 9	1.0	45	1.0	10	30	20-25	650	1.3	0.32
Ex. 10	1.0	45	0.78	10	12	30	1150	0.9	0.56
Ex. 11	1.05	45	3.0	25	21.25	25-28	900	0.9	0.48
Ex. 12	1.5	46	0.61	10	8.0	50	2250	0.9	9.8
Ex. 13	0.7	35	0.5	10	4.0	30	210	1.0	0.24
Ex. 14	0.5	35	0.5	10	2.75	30	200	0.8	0.14
Ex. 15	0.6	35	0.5	10	3.5	30	218	0.9	0.14
Ex. 16	1.0	35	0.5	10	8.25	30	202	1.1	1.01
Ex. 17	1.1	45	0.1	15	15	25-30	635	---	0.96
Resin A								0.9	13.8
Resin B								1.0	9.7

1- Epichlorohydrin addition time in hours.

2- Temperature maintained during epichlorohydrin addition.

3- Epichlorohydrin reaction time in hours.

4- Temperature maintained during epichlorohydrin reaction.

5- Final viscosity in centipoise.

6- Wet tensile ratio as defined in Example 18.

Table II

Effect of PAA Base Viscosity on PAE Resin Performance

PAA BASE					PAE RESIN			
I.D	TA[1]	%Solids	pH	Visc.[2]	E/N	WET[3]	% W/D[4]	R[5]
1	290	50	9.8	375	1.0	1.7	14	0.77
2	277	50	9.7	765	1.0	1.9	15	0.86
3	280	50	10	925	1.0	2.1	17	0.97

1. Total alkalinity based on solids
2. Brookfield (Spindle #2, @ 12 RPM) viscosity of a 50% aqueous solution in cps
3. Wet tensile of sheet treated with PAE resin
4. Wet tensile/dry tensile x 100%
5. Wet tensile ratio defined in Example 18.

Example 19

Total Organically Bound Chlorine Analysis

Extraction-G.C. Method

1. Sample Preparation

Approximately 5.000 g of the wet strength resin composition according to the invention comprised of an aminopolyamide-epichlorohydrin acid salt resin was added into a 40ml screw-top centrifuge tube. About 25 ml of ethyl acetate was added and the contents of the centrifuge tube were shaken thoroughly until the resin solution was dispersed. The contents of the tube were allowed to stand for 5 min. and then shaken again. The contents of the tube were centrifuged at high speed for 10 min. or until the upper solvent layer was clear. A portion of the supernatant solution was taken for G.C. injection.

2. Preparation of Standards

Stock solutions of approximately 1000 ppm of epichlorohydrin, 1,3-dichloro-2-propanol, and 3-chloro-1,2-propanediol were prepared in ethyl acetate on a weight to weight basis. These were further diluted volumetrically to lower levels prior to use. The second dilution depended upon the anticipated concentrations of the level of organic

chlorides in the aminopolyamide-epichlorohydrin resin solutions.

3. Gas Chromatographic Conditions

Detector: electron capture

Column: 0.54 mm capillary column, polyethylene glycol stationary phase, 2.5 micron film thickness. Septum purge: 0.5 minute

Carrier gas: He, 10 psi head pressure

Makeup gas: Nitrogen at 40 psi

Because of the differences between the retention times of epichlorohydrin and chloropropanediol, optimum integration of all peaks was achieved when the analysis was done in two steps. The best values for 1,3-dichloro-2-propanol, and 3-chloro-1,2-propanediol resulted from an isothermal run at 190°C and for epichlorohydrin, a ramped program from 120°C-190°C was used.

4. Calculations

The concentration of organically bound chlorine in the extract was calculated from the formula:

$$Conc.\ of\ Extract = \frac{Conc.\ of\ Stnd.}{Response\ of\ Stnd.} X\ Response\ of\ Extract$$

The resulting concentration in the extract was multiplied by the ratio of ethyl acetate to aminopolyamide-epichlorohydrin samples used in the extraction to give the concentration of organically bound chlorine in the original sample.

Example 20.

Preparation of A Composition Containing 1,2-propylene glycol.

To a round bottom flask were charged 115 grams of a 45.2% solids aminopolyamide resin solution having a total alkalinity based on solids content (TA) of 292.9 mg KOH/g, 78.6 grams of 1,2-propylene glycol, and 3.3 grams of water. Gentle stirring was applied and the contents of the flask

were cooled to about 10°C (ECH addition temperature) at which time about 25.2 grams of epichlorohydrin were added over 25 minutes. After completion of the epichlorohydrin addition, the contents of the reactor were allowed to exotherm to a temperature of about 30°C. The reaction mass was held at this temperature for 13 hours (ECH reaction temperature & time). The viscosity at this point (Final Visc.) was 1400 cps. The reaction was stopped by adjusting the pH of the solution to 2.0 with 37% hydrochloric acid. The resulting resin composition contained 31% 1,2-propylene glycol, 34% aminopolyamide-epichlorohydrin acid salt resin and 35% water. The viscosity was 763 cps.

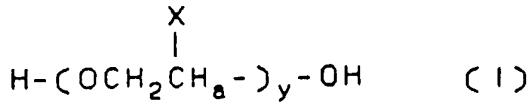
Example 21.

Preparation of A Composition Containing Methyl Carbitol.

To a round bottom flask were charged 113 grams of a 45.2% solids aminopolyamide resin solution having a total alkalinity based on solids content (TA) of 292.9 mg KOH/g, 78.6 grams of 1,2-propylene glycol, and 3.3 grams of water. Gentle stirring was applied and the contents of the flask were cooled to about 8°C (ECH addition temperature) at which time about 24.7 grams of epichlorohydrin were added over 10 minutes. After completion of the epichlorohydrin addition, the contents of the reactor were allowed to exotherm to a temperature of about 31°C. The reaction mass was held at this temperature for 9 hours (ECH reaction temperature & time). The viscosity at this point (Final Visc.) was 1325 cps. The reaction was stopped by adjusting the pH of the solution to 2.0 with 37% hydrochloric acid. The resulting resin composition contained 28% methyl carbitol, 32% aminopolyamide-epichlorohydrin acid salt resin and 40% water. The viscosity was 485 cps.

What is claimed is:

1. A composition comprising from about 10% to about 60% by weight of an aminopolyamide-epichlorohydrin acid salt resin; from about 5% to about 90% by weight of a solvent selected from the group consisting of a polyol wherein said polyol is an aliphatic compound having two or more hydroxyl groups and which is miscible with water; methyl or butyl carbitol; and a compound of the formula I



wherein X is H, CH_3, C_2H_5; a is 1 or 2; and y is less than 10; and up to about 85% by weight water.

2. The composition of claim 1 wherein the amount of said aminopolyamide-epichlorohydrin acid salt resin in said composition is about 10% by weight.

3. The composition of claim 1 wherein the amount of said aminopolyamide-epichlorohydrin acid salt resin in said composition is about 35% by weight.

4. The composition of claim 1 wherein the amount of said aminopolyamide-epichlorohydrin acid salt resin in said composition is about 45%.

5. The composition of claim 1 wherein the amount of aminopolyamide-epichlorohydrin acid salt resin in said composition is from about 30% to about 35% by weight, the amount of solvent in said composition is from about 20% to about 35% by weight, and the amount of water in said composition is from about 30% to about 50%.

6. The composition of claim 1 wherein said aminopolyamide-epichlorohydrin acid salt resin is comprised of less than about 0.7% by weight of total organically

bound chlorine.

7. The composition of claim 1 wherein said polyol is PEG 200.

8. The composition of claim 1 wherein said polyol is 1,2-propylene glycol.

9. The composition of claim 1 wherein said solvent is a mixture comprised of 10% by weight of 1,6-hexanediol and 90% by weight of butyl carbitol.

10. The composition of claim 1 wherein said aminopolyamide-epichlorohydrin acid salt resin is comprised of less than about 0.7% by weight of total organically bound chlorine.

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/US94/00127

A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :C08K 5/05; C08L 77/06
US CL :524/386, 389, 608
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 524/386, 389, 608

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Please See Extra Sheet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ---- Y	US, A, 4,940,615 (HAMMER et al) 10 JULY 1990, col. 5, lines 59-64, col. 6, lines 45-49, col. 6, lines 60-61, col. 7, line 45 to col 8, line 21 and col. 8, lines 38-55.	1-4, 8, 10 ---------- 1-10
Y,P	US, A, 5,239,047 (DEVORE et al) 24 AUGUST 1993, Claims 1-4.	1-10
Y,P	US, A, 5,256,727 (DULANY et al) 26 OCTOBER 1993, col. 3 line 39 to col. 4, line 65.	1-10
Y,P	US, A, 5,189,142 (DEVORE et al) 23 FEBRUARY 1993, Claims 1-4.	1-10
Y	US, A, 5,057,311 (KAMEGAI et al) 15 OCTOBER 1991, col. 3., lines 10-21 and col. 7, lines 35-42.	1, 2, 8, 10

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be part of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 07 MARCH 1994	Date of mailing of the international search report MAR 24 1994
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230	Authorized officer DONALD R. WILSON Telephone No. (703) 305-2351

Form PCT/ISA/210 (second sheet)(July 1992)*

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/US94/00127

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,402,748 (KILLAT et al) 06 SEPTEMBER 1983, col. 6, lines 55-58 and col. 8, lines 1-15.	1-10
Y	US, A, 4,563,376 (HAMMER et al) 07 JANUARY 1986, col. 4, lines 1-9.	1-10

B. FIELDS SEARCHED
Electronic data bases consulted (Name of data base and where practicable terms used):

APS
Search Terms: aminopolyamide or polyaminopolyamide
epichlorohydrin
propylene glycol or propyleneglycol or polypropylene glycol
ethylene glycol or ethyleneglycol or polyethylene glycol
butyl carbitol or butoxyethoxyethanol or 2-(2-butoxyethoxy)ethanol