

(19) World Intellectual Property  
Organization  
International Bureau



(43) International Publication Date  
28 October 2004 (28.10.2004)

PCT

(10) International Publication Number  
**WO 2004/092248 A1**

(51) International Patent Classification<sup>7</sup>: **C08G 73/02**,  
69/48, D21H 21/20

(21) International Application Number:  
PCT/US2004/009205

(22) International Filing Date: 24 March 2004 (24.03.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:  
10/404,940 1 April 2003 (01.04.2003) US

(71) Applicant (for all designated States except US): **HER-  
CULES INCORPORATED** [US/US]; Hercules Plaza,  
1313 North Market Street, Wilmington, DE 19894-0001  
(US).

(72) Inventor: **MASLANKA, William, W.**; 130 South Bank  
Road, Landenberg, PA 19350 (US).

(74) Agent: **SAMUELS, Gary, A.**; Hercules Incorporated,  
Hercules Plaza, 1313 North Market Street, Wilmington,  
DE 19894-0001 (US).

(81) Designated States (unless otherwise indicated, for every  
kind of national protection available): AE, AG, AL, AM,  
AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN,  
CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI,  
GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE,  
KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD,  
MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG,  
PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM,  
TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM,  
ZW.

(84) Designated States (unless otherwise indicated, for every  
kind of regional protection available): ARIPO (BW, GH,  
GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),  
Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), Euro-  
pean (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR,  
GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK,  
TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW,  
ML, MR, NE, SN, TD, TG).

**Published:**

— with international search report

For two-letter codes and other abbreviations, refer to the "Guid-  
ance Notes on Codes and Abbreviations" appearing at the begin-  
ning of each regular issue of the PCT Gazette.

(54) Title: SYNTHESIS OF HIGH SOLIDS RESINS FROM AMINE TERMINATED POLYAMIDES

(57) Abstract: The present invention contemplates a process for forming polyaminoamide polymers formed by the reaction of a dibasic acid/ester with excess amounts of an amine; the intermediate polymer resulting therefrom; a process for synthesizing effective, high solids resins resulting from the reaction of intermediate polymers with an epihalohydrin; and the resultant high, solids resin. These resins may be used as wet strength resins in the papermaking industry.



WO 2004/092248 A1

## SYNTHESIS OF HIGH SOLIDS RESINS FROM AMINE TERMINATED POLYAMIDES

5

### TECHNICAL FIELD AND INDUSTRIAL APPLICABILITY OF INVENTION

The present invention relates to a process for forming polyaminoamide polymers using excess amounts of an amine; the intermediate polymer resulting therefrom; a process for synthesizing effective, high solids wet strength resins; and the polyaminoamide resin resulting therefrom.

10

### BACKGROUND OF THE INVENTION

Polyaminoamide based resins have been used for over forty years in the manufacture of paper under neutral and alkaline conditions. Furthermore, in the paper industry, polyaminoamides made from dibasic acids and polyamines are commonly used as pre-polymers for the synthesis of polyaminoamide-epichlorohydrin (PAE) resins (e.g. H.H. Espy, *TAPPI J.*, 78, 90 (1995)). Typically, to result in a resin, a polyaminoamide is treated with epichlorohydrin, which reacts with the secondary amines in the polymer backbone to form chlorohydrin, azetidinium or epoxide functionalities necessary for self-crosslinking and reacting with the cellulosic pulp fiber as shown in U.S. Patents 2,926,116; 2,926,154; 3,332,901; 5,644,021; 6,222,006; and 5,668,246.

20

The procedures for making polyaminoamide-epichlorohydrin resins are well known in the art. However, with respect to making the polyaminoamides, typical processes produce polyaminoamides having a high molecular weight and a wide molecular weight distribution and are generally prepared using a 1:1 mole ratio of dibasic acid and polyamine. The high molecular weight of the polyaminoamide, when later converted to a resin, limits the level of solids at which the resin can be prepared and stored while still maintaining a high level of performance. As a result, the concentration of resin solids are in the range of about 10 wt.-% to about 30

25

30

wt.-% of the resin, but are generally limited to a maximum of about 30 wt.-%. At present, there is a need within the industry to provide high solids resins having the capacity to undergo long periods of storage while maintaining a level of performance substantially equal to those resins having a lowers solids content.

Recently, the approach to synthesizing high solids resins has involved reducing the molecular weight of the polyaminoamide via an endcapping technique using a monobasic acid to control the growth of the polymer chains and the molecular weight distribution. Conversion of such polyaminoamides to resins through reaction with epihalohydrins has produced resin solids as high as 40%. However these types of processes necessitate the handling of extra ingredients not required by the present invention. Thus, the present invention provides for a simpler, more efficient process than those currently used in the art.

There are several distinct advantages conferred by the present invention. First, the present invention allows one to control the molecular weight of the polyaminoamide via the increased polyamine:dibasic acid/ester mole ratio producing a low molecular weight polymer with a narrow molecular weight distribution. Second, the additional amine groups resulting from the increased polyamine: dibasic acid/ester mole ratio provide additional sites for reaction with epihalohydrin, thus giving potentially higher reactive functionality. Third, the combination of low molecular weight and a narrow molecular weight distribution allows for the synthesis of high solids resins having good storage stability and performance.

#### SUMMARY OF THE INVENTION

The present invention relates to a wet strength agent and creping aid useful in papermaking.

The present invention contemplates a process for the synthesis of a polyaminoamide intermediate polymer, as well as the intermediate polymer itself, comprising the steps of:

- (a) mixing an amount of a dibasic acid or ester and an excess amount of an amine, thereby forming a polymerization mixture; and
- (b) allowing the polymerization mixture from step (a) to polymerize to completion.

The present invention further contemplates a process for the synthesis of a high solids polyaminoamide resin, as well as the high solids resin itself, comprising the step of:

- (c) reacting the mixture from step (b) with an epihalohydrin; and
- (d) allowing the reaction to proceed wherein the intermediate polymer is cross-linked.

The present invention also relates to cellulosic products produced using a high solids resin of the present invention.

## DETAILED DESCRIPTION OF A PREFERRED EMBODIMENT OF THE INVENTION

The present invention contemplates a process for the synthesis of a polyaminoamide intermediate polymer, as well as the intermediate polymer itself, comprising the steps of:

- (a) mixing an amount of a dibasic acid or ester and an excess amount of an amine, wherein the dibasic acid/ester:amine mole ratio ranges from about 1:1.125 to about 1:1.175, thereby forming a polymerization mixture; and
- (b) allowing the polymerization mixture from step (a) to polymerize to completion.

The present invention further contemplates a process for the synthesis of a high solids polyaminoamide resin, as well as the high solids resin itself, comprising the step of:

- (c) reacting the mixture from step (b) with an epihalohydrin; and
- (d) allowing the reaction to proceed where the intermediate polymer is cross-linked.

The polyaminoamide synthesis is generally carried out neat although some water may be added to facilitate mixing of the monomers (10-20% based on monomers) and removed with the water of polycondensation.

5           The amount of the dibasic acid or ester and the excess amount of the amine utilized to form the polymerization mixture of the present invention are defined by the comonomer ratio. The comonomer, in turn, is determinative of the intermediate polymer's molecular weight. The molecular weight of the intermediate polymer varies according to the  
10 reaction temperature, the specific monomers used for the reaction, their ratio and the reaction time. The molecular weight and distribution are determined by Size Exclusion Chromatography, a technique that discriminates materials based primarily on the size of the molecules. Controlling the dibasic acid/ester:amine mole ratio, particularly through the  
15 use of excess amounts of the amine allows for the control of the molecular weight, as well as the narrow molecular weight distribution. Typically the excess amount of the amine ranges from about 10 to about 20%, when compared to the amount of dibasic acid/ester utilized, preferably between about 12.5% and about 17.5%. Thus in terms of defining the relationship  
20 between molecular weight and comonomer ratio, a dibasic acid/ester:amine mole ratio of about 1:1 generally corresponds to a number average molecular weight ( $M_n$ ) ranging from about 3000 to about 3500 Daltons. However, in the present invention the dibasic acid/ester:amine mole ratio preferably ranges from about 1:1.175 to about  
25 1:1.125, which generally corresponds to a low number average molecular weight and narrow weight distribution of about 1600 to about 2100 Daltons and a polydispersity ( $M_w/M_n$ ) ranging from about 1.5 to about 2. The amine number on a dry basis for the polyaminoamide ranges from 6.1-6.7 meq/g. In addition the polymer mixture has a solids content of the  
30 intermediate polymer generally ranging from about 30 wt.-% to about 70 wt.-%, preferably about 48-50 wt.-%.

In the process of the present invention, step (a) is an exothermic reaction owing to salt formation when the polyamine and dibasic acid are mixed and therefore, the reaction vessel should be cooled through any suitable means known in the art to prevent any loss of monomers.

- 5 Preferably, this reaction temperature of step a) should be controlled so it remains below about 110°C. The rate of addition may be performed at any rate so long as the reaction temperature stays below the cited temperature. After the addition is completed, the polycondensation itself is carried out at about 169-171°C. In general, there is no particular sequence  
10 required for mixing the components of step a), however, the polyamine is preferably charged first followed by the dibasic acid or ester.

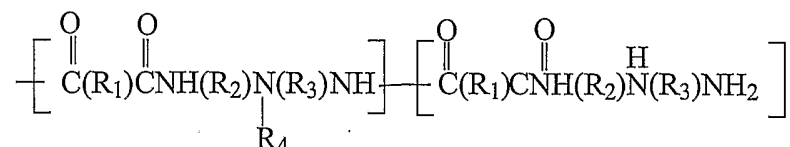
- The reaction time is partially determinative of the molecular weight of the intermediate polymer, wherein a longer reaction time generally corresponds to a higher molecular weight. The reaction time can be  
15 adjusted to provide an intermediate polymer having the appropriate molecular weight for the desired application. Typically, at the beginning of the reaction the polymerization mixture may be pasty, but as the polymerization reaction proceeds, the contents of the reaction vessel become clear and the viscosity increases. A sample can be withdrawn  
20 from the polymerization mixture, and the viscosity determined. In general, the formation of the appropriate intermediate polymer results in a clear solution after water addition having a Brookfield viscosity of about 135-195 cps, and preferably 150-180 cps.

- The resultant intermediate polymer has the combination of a reduced  
25 molecular weight and a narrow weight range distribution, which when later reacted with an epihalohydrin provides a high solids resin with good storage stability and good wet-strength and creping performance. The intermediate polymer of the present invention also contains additional amine groups, thereby providing additional sites for reaction with an  
30 epihalohydrin. For example, as shown in Examples 1,2 and 3 with respect to DETA, as the amount of excess DETA utilized in the present invention increases, the amine number also increases. The increased number of

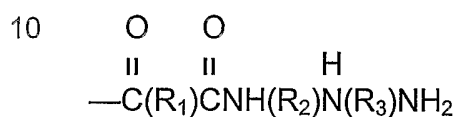
amine groups may be shown using amine analysis, a well known technique within the art.

According to the present invention, the intermediate polymer resulting from step (b) may be either a linear or a branched condensation polymer.

- 5 In a general and representative sense, the intermediate polymer, also contemplated by the present invention, has the general formula:

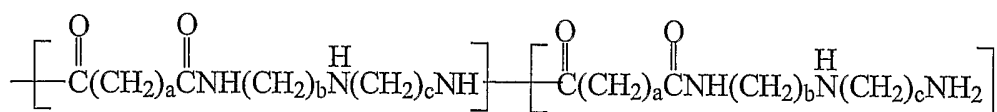


wherein  $\text{R}_1$  ranges from  $\text{C}_2\text{-C}_8$ ;  $\text{R}_2$  ranges from  $\text{C}_2\text{-C}_6$ ;  $\text{R}_3$  ranges from  $\text{C}_2\text{-C}_6$ , and  $\text{R}_4$  is



- For example, the linear polymer structure from the reaction product of  
15 adipic acid and DETA would be:

LINEAR

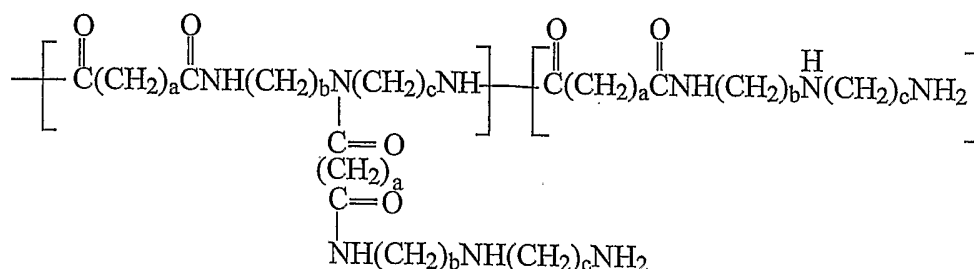


wherein  $a$  ranges from 2-8,  $b$  ranges from 2-6 and  $c$  ranges from 2-6.  
Preferably,  $a$  ranges from 2-6,  $b$  ranges from 2-4 and  $c$  ranges from 2-4;  
more preferably  $a$  is 3-4,  $b$  is 2-3 and  $c$  is 2-3.

- One of the possible branch structures from the same reaction is  
20 given as

follows:

BRANCHED

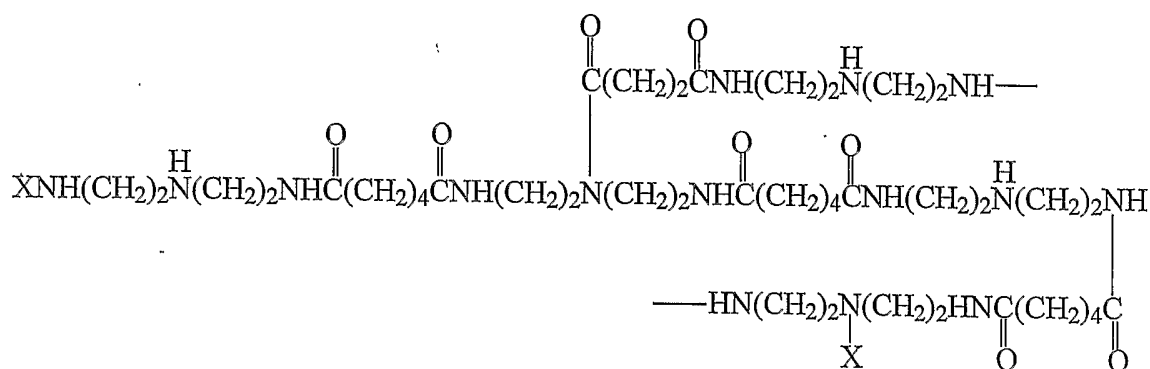


wherein a ranges from 2-8, b ranges from 2-6 and c ranges from 2-6.

Preferably, a ranges from 2-6, b ranges from 2-4 and c ranges from 2-4;

5 more preferably a is 3-4, b is 2-3 and c is 2-3.

Generally, the structure resulting from processes known in the art utilizing the endcapping method is as follows:



10



wherein X is  $\text{RC}—$ , and R is methyl, ethyl and the like.

Examples of suitable dibasic acids include, but are not limited to, adipic acid, glutaric acid, succinic acid, azelaic acid, sebacic acid, maleic

acid, fumaric acid, itaconic acid, oxalic acid and mixtures thereof. Dibasic acids having 4-8 carbons are preferred.

Examples of suitable dibasic esters include, but are not limited to, dimethyladipate, dimethylsebacate, dimethylitaconate, dimethylazelaate,  
5 dimethyloxalate, dimethylglutarate and mixtures thereof. The dibasic esters suitable for the present invention may be prepared by any known alcohol known in the art, for example, ethanol, propanol, butanol, pentanol, hexanol, isopropanol, benzyl alcohol, phenol and the like and mixtures thereof.

10 The polyamine functions to control the growth of polyamide chains reducing the molecular weight and narrowing the distribution. Examples of suitable diamines contemplated by the present invention include, but are not limited to, diethylene triamine (DETA) or its analogs, N-(3-aminopropyl)-1,3-propanediamine (dipropylene triamine or DPTA),  
15 ethylene diamine (EDA), 1,6-hexamethylenediamine (HMDA), triethylene tetraamine (TETA), tetraethylene pentaamine (TEPA), N-methyl-bis(aminopropyl)amine (MBAPA), bis(hexamethylene triamine) (BHMT), tripropylene tetraamine, tetrapropylene pentaamine, spermine, spermidine,  
20 1-phenyl-2,4-pentane diamine, 2-phenyl-1,3-propanediamine, 2-methyl-1,5-pentane diamine, and phenylene diamine and combinations thereof. The preferred diamines are diethylene triamine (DETA), triethylene tetraamine (TETA), tetraethylene pentaamine (TEPA) and combinations thereof. The most preferred diamine is diethylene triamine (DETA).

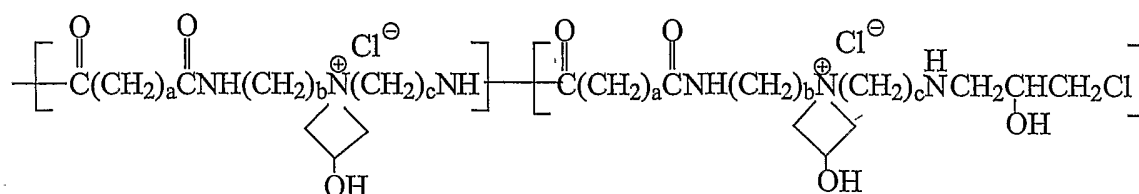
The present invention further contemplates reacting the  
25 intermediate polymer with an epihalohydrin, preferably epichlorohydrin, thereby resulting in a high solids polyamide resin, wherein the polymer has the ability to cross-link with itself or to react with other materials, such as paper, pulp, wool, wood and the like. When the polymers of the present invention are treated with epichlorohydrin under the appropriate reaction  
30 conditions (i.e., those conditions shown in the Examples are preferred), the resulting resins are water-soluble, cationic resins. The resin synthesis is most commonly carried out in water (40-44 wt.-% solids before dilution

to the final solids content percentage). The epichlorohydrin:polyaminoamide ratio is based on the amine number in the polymer (e.g. the epi:amine equivalents). The epichlorohydrin:amine equivalent ratio ranges from 1:1 to 1:1.3, preferably 1:1.2 to 1:1.25. The  
5 high solids resins according to the present invention generally have a solids content, of the intermediate polymer and epichlorohydrin, in the range of about 30-50 wt.-%, preferably in the range of about 30-45 wt.-% and more preferably about 39-41 wt.-%.

The reaction time varies depending upon the reaction temperature,  
10 where lower temperatures generally require longer reaction times. The reaction is preferably carried out until all or substantially all of the available amine groups are reacted with the epichlorohydrin. Manipulation of temperatures aid in determining the functionality of the resin, for example, in reacting the intermediate polymer with an epichlorohydrin, it may occur at  
15 a temperature up to about 70°C, wherein the temperature may remain constant throughout the reaction or it may be multi-staged such that a low temperature is used initially and subsequently utilizes an elevated temperature. At a predetermined terminal viscosity water may be added to adjust the resin's solids content and the pH adjusted to about 2.7-3.3,  
20 preferably about 2.8 –3.0, preferably using a combination of sulfuric and formic acids. These types of resins may be used as wet strength resins and/or creping aids in papermaking processes.

According to the present invention, the high solids resin may have either a linear or branched structure. In a general and representative  
25 sense, the high solids resin, also contemplated by the present invention, has the general linear formula:

## LINEAR



wherein a ranges from 2-8, b ranges from 2-6 and c ranges from 2-6.

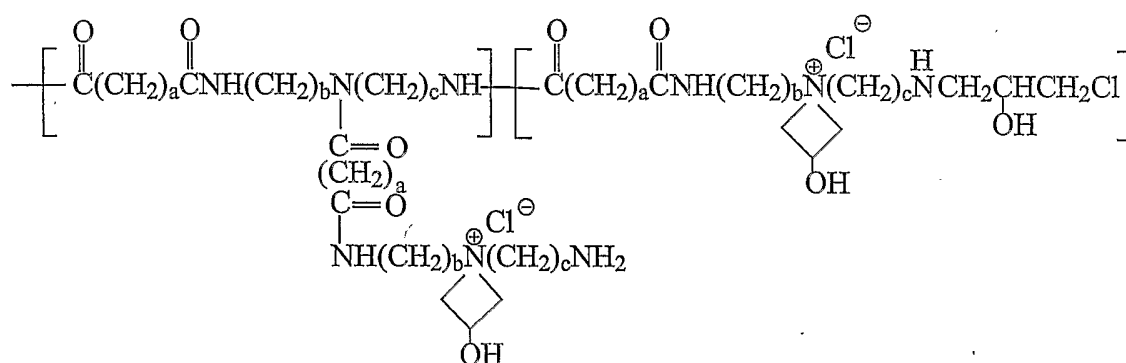
Preferably, a ranges from 2-6, b ranges from 2-4 and c ranges from 2-4:

more preferably a is 3-4, b is 2-3 and c is 2-3.

A general branched structure is given as follows:

5

## BRANCHED



wherein a ranges from 2-8, b ranges from 2-6 and c ranges from 2-6.

Preferably, a ranges from 2-6, b ranges from 2-4 and c ranges from 2-4;

more preferably a is 3-4, b is 2-3 and c is 2-3.

The present invention provides resins having superior storage stability when compared to those resins utilizing high molecular weight polyaminoamides. Typically, a resin contemplated by the present invention having a solids content of about 40% and stored at about 25°C (77°F) to about 32°C (90°F) will remain stable to gelation (visual observation) for about 3 to about 6 weeks.

15           The present invention further contemplates cellulosic products  
produced using a high solids resin of the present invention in any

conventional process typically utilized to produce cellulosic products such as paper towels, napkins, writing paper, and the like. The resin may be incorporated into cellulosic products in an amount generally ranging from about 0.25% to about 3%, wherein for paper the amount ranges from  
5 about 0.25% to about 1.5%; wherein for napkins the amount ranges from about 0.25% to about 1.0%; and wherein for paper towels the amount ranges from about 0.5% to about 1.5%; based on the dry weight of the paper. The quantity of resin added to aqueous paper stock is dependent upon the degree of wet strength desired and the amount of resin retained  
10 by the paper fibers. The paper, either preformed or partially dried, can be impregnated by immersion in the resin or by spraying the resin onto the paper. Subsequently, the paper can be heated for about 5 to about 30 minutes at temperatures of about at least 80°C in order to fully cure the resin.

15 The embodiments of the present invention are further defined in the following Examples. It should be understood that these Examples are given by way of illustration only. From the above discussion and these Examples, one skilled in the art can ascertain the essential characteristics of this invention, and without departing from the spirit and scope thereof,  
20 can make various changes and modifications of the invention to adapt it to various uses and conditions. Thus various modifications of the present invention in addition to those shown and described herein will be apparent to those skilled in the art from the foregoing description. Although the invention has been described with reference to particular means, materials  
25 and embodiments, it is to be understood that the invention is not limited to the particulars disclosed, and extends to all equivalents within the scope of the claims.

## EXAMPLES

30 The polyaminoamides for Examples 1, 2 and 3 were made as set forth below, where the varying factor was the excess amount of DETA utilized in the reaction. The storage stability was tested by storing the

resins at 90°C for a period of 6 weeks. Stability is determined by assessing whether gelation has occurred in the mixture (visual observation or comparison to Gardner-Holdt standards at 25°C).

5 Comparative Example – C

Comparative Example (C) shows the data for a lower solids, high molecular weight polyaminoamide, where the dibasic acid/ester:amine ratio was 1:1. This Comparative Example was prepared in the same manner as Examples 1,2 and 3 except for the utilization of the 1:1 dibasic  
10 acid/ester:amine ratio.

Examples 1, 2 and 3: Copolymerization of Adipic Acid and Diethylenetriamine (12.5%, 15% and 17.5% Excess DETA)

Diethylenetriamine (174.2g, 1.69 moles) was charged to the  
15 reaction vessel. Adipic acid (219.2g, 1.5 moles) was cautiously added keeping the temperature below 110°C. After the addition was complete, the contents of the reaction vessel were heated to 169-170°C and the water from the poly condensation removed by distillation. Total hold time at this temperature was 180 minutes. Dilution water was added and the  
20 polyaminoamide was stirred until dissolved, in order to attain the desired solids content.

Total solids = 48.5%

Brookfield viscosity = 211 cps

pH = 10.7

25 Reduced viscosity = 0.102 dL/g (1MNH<sub>4</sub>Cl, 2%, 25°C)

Mn = 2273 Daltons

Mw = 4223

Mz = 6899

Mw/Mn = 1.96

30 Amine No. = 2.98 meq/g

Acid No. = 0.106 meq/g

Table 1: Polyaminoamides made from adipic acid and excess  
diethylenetriamine

Ex.	Mole Ratio*	Total Solids (%)	Brookfield Viscosity	pH	RV (dL/g)	Amine No. (meq/g)	Acid No. (meq/g)	Mn	Mw	Mw/Mn
C	1:1	49.3	457 cps	10.2	0.138	2.6	0.14	3200	7260	2.27
1	1:1.125	48.0	177 cps	10.5	0.100	3.00	0.133	1915	3499	1.83
2	1:1.15	48.2	168 cps	10.5	0.096	3.24	0.15	2026	3621	1.79
3	1:1.175	48.2	169 cps	10.8	0.092	3.22	0.11	1642	2862	1.74

5 \* The mole ratio is the ratio of the dibasic acid/ester:amine

The amine numbers and acid numbers in Table 1 are shown "as received". The true amine number for Examples 1, 2 and 3 and Comparative Example C are determined by dividing the value shown in  
10 Table 1 by the total solids value as shown in Table 2.

Table 2: Adjusted Amine and Acid Number Values

Example	Amine No.	Acid No.
C	5.27	0.28
1	6.25	0.28
2	6.72	0.31
3	6.68	0.23

Example 4: Synthesis of a Resin Using a Polyaminoamide Prepared with  
Excess Diethylenetriamine (12.5%)

15 Poly (adipic acid-co-diethylenetriamine) (12.5 mole% excess DETA) (80g, 166.7g, 48% solution, 0.50 equivalent amine) was charged to the reaction vessel and diluted to a total weight of 255.4g. Epichlorohydrin (57.8g, 0.625 equivalent) was added all at once. The temperature was raised to 68-70°C and the viscosity was monitored. At Gardner-Holdt "U/V"  
20 31cc of cold water was added and concentrated H<sub>2</sub>SO<sub>4</sub> was added to bring

the pH to 4.8. 25% HCOOH was then added to lower the pH to 3.7 and the pH trimmed to 3.25 with additional concentrated H<sub>2</sub>SO<sub>4</sub>.

Total solids = 39.4%

Brookfield viscosity = 368 cps

5 GC

Epichlorohydrin = 0.029%

1,3 Dichloropropanol = 2.48%

2,3 Dichloropropanol = 81 ppm

3 Chloropropanediol = 0.27%

10 90°F stability = >6 weeks

Example 5: Synthesis of a Resin Using a Polyaminoamide Prepared with Excess Diethylenetriamine (15%)

15 Poly (adipic acid-co-diethylenetriamine) (15 mole% excess DETA) (24.4g, 154.3g, 48.2% solution, 0.5 equivalent amine) was charged to the reaction vessel and diluted to a total weight of 242.7g. Epichlorohydrin (57.8g, 0.625 equivalent) was added all at once. The temperature was raised to 68-70°C and the viscosity monitored. At Gardner-Holdt "U/V" 31cc of cold water was added, followed by concentrated H<sub>2</sub>SO<sub>4</sub> to bring  
20 the pH to 4.8. 25% HCOOH was then added to lower the pH to 3.7 and the pH finally trimmed to 3.25 with additional concentrated H<sub>2</sub>SO<sub>4</sub>.

Total solids = 39.5%

Brookfield viscosity = 297 cps

GC

25 Epichlorohydrin = 0.006%

1,3 Dichloropropanol = 2.64%

2,3 Dichloropropanol = 157 ppm

3 Chloropropanediol = 0.44%

90°F stability = >6 weeks

30

Example 6: Synthesis of a Resin Using a Polyaminoamide Prepared with Excess Diethylenetriamine (17.5%)

Poly (adipic acid-co-diethylenetriamine) (17.5 mole% excess DETA) (75.3g, 156.3g, 48.2% solution, 0.5 equivalent amine) was charged to the reaction vessel and diluted to a total weight of 244.7g. Epichlorohydrin (57.8g, 0.625 equivalent) was added all at once. The temperature was raised to 68-70°C and the viscosity monitored. At Gardner-Holdt "U/V" 30cc of cold water was added, followed by concentrated H<sub>2</sub>SO<sub>4</sub> to bring the pH to 4.8. 25% HCOOH was then added to lower the pH to 3.77 and finally the pH was trimmed to 3.2 with additional concentrated H<sub>2</sub>SO<sub>4</sub>.

Total solids = 40.1%

Brookfield viscosity = 331 cps

GC

Epichlorohydrin = 0.008%

1,3 Dichloropropanol = 2.44%

2,3 Dichloropropanol = 0.009%

3 Chloropropanediol = 0.028%

90°F stability = >6 weeks

Example 7: Handsheet Evaluation of Resins

The resins of Examples 4, 5, 6, as well as Kymene®557H wet strength resin, were evaluated in handsheets prepared from 50/50 blends of hardwood/softwood pulp beaten to a consistency of 2-2.5% in a cycle beater to 450cc Canadian Standard Freeness at pH 7.5. Table 2 summarizes the results from the handsheet evaluation.

The percent resin incorporated into the handsheets was 0.5% (w/w) based on pulp fiber. Kymene® 557H (a polyamidoamine-epichlorohydrin wet strength agent supplied by Hercules, Incorporated of Wilmington, DE) was used as the control. The percent resin is determined by adding resin (solid) based on dry pulp, (e.g. at 0.5% add-on to 50 grams of dry pulp in a slurry, 0.25 grams of resin would be added on a dry basis). The resin was

then formed into handsheets having a basis weight of 40 lbs/ream (24" x 36", 500 sheets) The sheets were dried to a moisture content of about 6%.

The handsheets were cured for 30 minutes at 80°C. The handsheets were tested for both dry strength and wet strength (after  
5 soaking in 20°C distilled water for 2 hours).

The dry tensile strength and wet tensile strength were determined by the exertion of tension on the 1" wide paper strip being tested at a rate of 2-3" per minute and the maximum tensile strength was observed upon failure (TAPPI METHOD 494). The "% level" indicates the amount of resin  
10 utilized, based on the weight of the pulp.

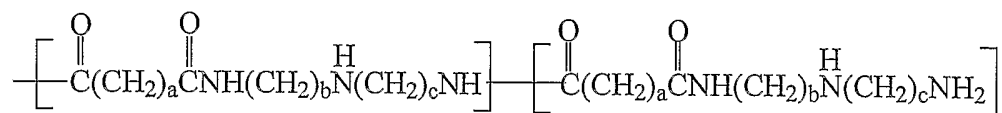
Table 3: Handsheet Evaluation Results

Resin	% Level	Basis Weight	Tensile (lbs./inch)	
			Cured Dry 80°C/30 min.	Cured Wet 80°C/30 min.
Example 4	0.25	40	20.7	3.92
	0.50	40	23.0	4.67
	1.0	40	21.6	5.32
Example 5	0.25	40	21.1	3.48
	0.50	40	22.3	4.30
	1.0	40	21.6	4.92
Example 6	0.25	40	21.3	3.55
	0.50	40	22.9	4.33
	1.0	40	22.1	4.71
Kymene 557H	0.25	40	22.2	3.69
	0.50	40	23.1	4.53
	1.0	40	22.4	5.33

## WHAT IS CLAIMED IS:

1. A process for the synthesis of an intermediate polyamide polymer comprising:
  - (a) mixing an amount of a dibasic acid or ester and an excess amount of an amine, wherein the diacid/ester:amine mole ratio ranges from about 1:1.125 to about 1:1.175, thereby forming a polymerization mixture; and
  - (b) allowing the polymerization mixture from step (a) to polymerize to completion.
2. The process according to claim 1, wherein the dibasic ester comprises at least one of dimethyladipate, dimethylsebacate, dimethylitaconate, dimethylazelate, dimethyloxalate, dimethylglutarate and mixtures thereof.
3. The process according to claim 1, wherein the dibasic acid comprises at least one of adipic acid, glutaric acid, oxalic acid, succinic acid, azelaic acid, sebacic acid, maleic acid, fumaric acid, itaconic acid and mixtures thereof.
4. The process according to claim 1, wherein the amine comprises at least one of diethylene triamine (DETA) or its analogs, N-(3-aminopropyl)-1,3-propanediamine (dipropylene triamine or DPTA), ethylene diamine (EDA), 1,6-hexamethylenediamine (HMDA), triethylene tetraamine (TETA), tetraethylene pentaamine (TEPA), N-methyl-bis(aminopropyl)amine (MBAPA), bis(hexamethylene triamine) (BHMT), tripropylene tetraamine, tetrapropylene pentaamine, spermine, spermidine, 1-phenyl-2,4-pentane diamine, 2-phenyl-1,3-propanediamine, 2-methyl-1,5-pentane diamine, and phenylene diamine and combinations thereof.
5. The process according to claim 4, wherein the amine comprises at least one of diethylene triamine (DETA), triethylene tetraamine (TETA), tetraethylene pentaamine (TEPA) and combinations thereof.

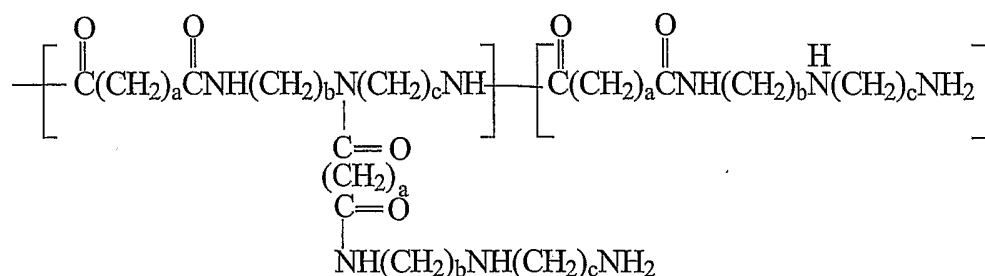
6. The process according to claim 5, wherein the amine is diethylene triamine (DETA).
7. The process according to claim 1, wherein the intermediate polymer has a molecular weight ranging from about 1600 to about 2100 Daltons.
8. The process according to claim 1, wherein the intermediate polymer is a water-soluble linear condensation polymer.
9. The process according to claim 1, wherein the intermediate polymer is a water-soluble branched condensation polymer.
10. An intermediate polymer reaction product produced according to the process of claim 1.
11. An intermediate polymer having a linear formula comprising:



wherein a ranges from 2-8, b ranges from 2-6 and c ranges from 2-6.

12. An intermediate polymer having a branched formula comprising:

## BRANCHED



wherein a ranges from 2-8, b ranges from 2-6 and c ranges from 2-6.

13. A process for making a high solids polyamide resin comprising:
  - (a) mixing an amount of a dibasic acid or ester and an excess amount of an amine, wherein the dibasic acid/ester:amine mole ratio ranges from about 1:1.125 to about 1:1.175, thereby forming a polymerization mixture;
  - (b) allowing the polymerization mixture from step (a) to polymerize to completion;
  - (c) reacting the polymerization mixture with an epihalohydrin; and
  - (d) allowing the reaction to proceed wherein the intermediate polymer reaction mixture is cross-linked.
14. The process according to claim 13, wherein the diester comprises at least one of dimethyladipate, dimethylsebacate, dimethylitaconate, dimethylazelaate, dimethyloxalate, dimethylglutarate and mixtures thereof.
15. The process according to claim 13, wherein the dibasic acid comprises at least one of adipic acid, glutaric acid, oxalic acid, succinic acid, azelaic acid, sebacic acid, maleic acid, fumaric acid, itaconic acid and mixtures thereof.
16. The process according to claim 13, wherein the amine comprises at least one of diethylene triamine (DETA) or its analogs, N-(3-aminopropyl)-1,3-

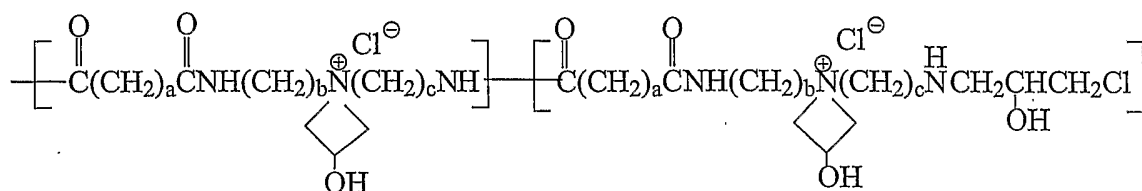
propanediamine (dipropylene triamine or DPTA), ethylene diamine (EDA), 1,6-hexamethylenediamine (HMDA), triethylene tetraamine (TETA), tetraethylene pentaamine (TEPA), N-methyl-bis(aminopropyl)amine (MBAPA), bis(hexamethylene triamine) (BHMT), tripropylene tetraamine, tetrapropylene pentaamine, spermine, spermidine, 1-phenyl-2,4-pentane diamine, 2-phenyl-1,3-propanediamine, 2-methyl-1,5-pentane diamine, and phenylene diamine and combinations thereof.

17. The process according to claim 16, wherein the amine comprises at least one of diethylene triamine (DETA), triethylene tetraamine (TETA), tetraethylene pentaamine (TEPA) and combinations thereof.
18. The process according to claim 17, wherein the amine is diethylene triamine (DETA).
19. The process according to claim 13, wherein the epihalohydrin is epichlorohydrin.
20. The process according to claim 13, wherein the high solids resin has a solids content in the range of about 30-50 wt.-%.
21. The process according to claim 20, wherein the high solids resin has a solids content in the range of about 30-45 wt.-%.
22. The process according to claim 21, wherein the high solids resin has a solids content in the range of about 39-41 wt.-%.
23. The process according to claim 13, wherein the intermediate polymer of step b) is cross-linked with itself.
24. The process according to claim 13, wherein the intermediate polymer of step b) is cross-linked with another material.

25. A high solids polyamide resin produced according to the process of claim 13.

26. A high solids polyamide resin having a linear formula comprising:

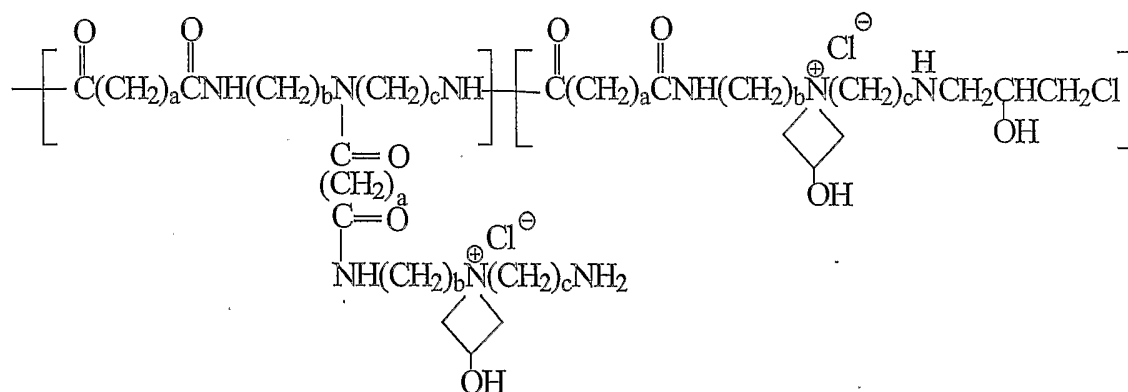
LINEAR



wherein a ranges from 2-8, b ranges from 2-6 and c ranges from 2-6.

27. A high solids polyamide resin having a branched formula comprising:

BRANCHED



wherein a ranges from 2-8, b ranges from 2-6 and c ranges from 2-6.

28. A wet strength agent produced by the process of claim 13.

29. A creping aid produced by the process of claim 13.

30. A cellulosic product comprising the resin of claim 26.

31. A cellulosic product comprising the resin of claim 27.

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US2004/009205

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08G73/02 C08G69/48 D21H21/20

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)

IPC 7 C08G D21H

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 practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 00/77076 A (HERCULES INC) 21 December 2000 (2000-12-21) page 6, line 31 - page 9, line 2 page 14, line 11 - page 17, line 13 page 31, line 6 - page 36, line 18 page 37, lines 5-20 page 39, lines 19-27 page 41, line 29 - page 43, line 4; claims 147-291; examples 25,28,35,38 -----	1-31
X	EP 0 802 215 A (HERCULES INC) 22 October 1997 (1997-10-22) page 2, line 3 - page 4, line 19 page 5, line 4 - page 8, line 3; claims; example 11 ----- -/--	1-31

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*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)
- \*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

- \*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
- \*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
- \*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.
- \* & \* document member of the same patent family

Date of the actual completion of the international search

27 July 2004

Date of mailing of the international search report

04/08/2004

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Otegui Rebollo, J

## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US2004/009205

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 222 006 B1 (KOKKO BRUCE JEROME ET AL) 24 April 2001 (2001-04-24) cited in the application column 2, lines 30-42 column 5, line 36 - column 8, line 22 column 9, line 39 - column 15, line 61; claims; examples 1-4 -----	1-31
X	GB 1 401 244 A (HERCULES INC) 16 July 1975 (1975-07-16) page 1, lines 12-16 page 2, line 26 - page 3, line 79; claims -----	1-31
X	US 2 926 154 A (KEIM GERALD I) 23 February 1960 (1960-02-23) cited in the application column 1, line 28 - column 2, line 69; example 7 column 6, lines 44-58; claims -----	1-31
X	EP 0 374 938 A (SUMITOMO CHEMICAL CO) 27 June 1990 (1990-06-27) page 2, line 11 - page 3, line 54; claims; example 7 -----	1-31

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US2004/009205

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 0077076	A	21-12-2000	AU 755277 B2	05-12-2002
			AU 5453400 A	02-01-2001
			CA 2375694 A1	21-12-2000
			CN 1355822 T	26-06-2002
			EP 1189972 A1	27-03-2002
			JP 2003502463 T	21-01-2003
			WO 0077076 A1	21-12-2000
			US 2003205345 A1	06-11-2003
			US 6554961 B1	29-04-2003
			ZA 200200279 A	11-04-2003
EP 0802215	A	22-10-1997	US 5786429 A	28-07-1998
			AU 730617 B2	08-03-2001
			AU 1894297 A	23-10-1997
			BR 9701851 A	29-09-1998
			CA 2202419 A1	18-10-1997
			DE 69725042 D1	30-10-2003
			DE 69725042 T2	08-07-2004
			EP 0802215 A1	22-10-1997
			ES 2202515 T3	01-04-2004
			US 5902862 A	11-05-1999
US 6222006	B1	24-04-2001	AU 8781998 A	08-03-1999
			CA 2268470 A1	25-02-1999
			EP 0931197 A1	28-07-1999
			TR 9900809 T1	21-05-2001
			WO 9909252 A1	25-02-1999
GB 1401244	A	16-07-1975	AR 195179 A1	19-09-1973
			AU 467644 B2	11-12-1975
			AU 4541972 A	14-02-1974
			BE 787371 A1	09-02-1973
			CA 979579 A1	09-12-1975
			CH 547327 A	29-03-1974
			DE 2239647 A1	22-02-1973
			ES 405785 A1	16-01-1976
			FR 2148630 A1	23-03-1973
			IT 963954 B	21-01-1974
			JP 48028098 A	13-04-1973
			JP 52029795 B	04-08-1977
			NL 7209216 A	14-02-1973
			ZA 7205475 A	25-04-1973
US 2926154	A	23-02-1960	US 2926116 A	23-02-1960
			US 3049469 A	14-08-1962
			DE 1546369 A1	21-05-1970
			DE 1177824 B	
			FR 1265829 A	07-07-1961
			GB 865727 A	19-04-1961
			NL 110447 C	
			NL 231136 A	
			US 3483077 A	09-12-1969
EP 0374938	A	27-06-1990	US 1476116 A	04-12-1923
			JP 2170825 A	02-07-1990
			JP 2969636 B2	02-11-1999
			DE 68917698 D1	29-09-1994
			DE 68917698 T2	15-12-1994

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No  
PCT/US2004/009205

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0374938	A	DK 666489 A	24-06-1990
		EP 0374938 A1	27-06-1990
		FI 98632 B	15-04-1997
		US 5017642 A	21-05-1991
<hr/>			