



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(54) Title:</b> THERMALLY STABLE POLYETHERAMINES		
<b>(57) Abstract</b>  <p>A laminate structure comprises one or more layers of an organic polymer and one or more layers of a hydroxy-functionalized polyetheramine, wherein the hydroxy-functionalized polyetheramine layer is adhered directly to a contiguous organic polymer layer without an adhesive layer therebetween. The hydroxy-functionalized polyetheramine is prepared by reacting (1) a difunctional amine with (2) a diglycidyl ether or diepoxy-functionalized poly(alkylene oxide) under conditions sufficient to cause the amine moieties to react with the epoxy moieties to form a polymer backbone having amine linkages, ether linkages and pendant hydroxyl moieties and then treating the reaction product with a monofunctional nucleophile which is not a primary or secondary amine.</p>		

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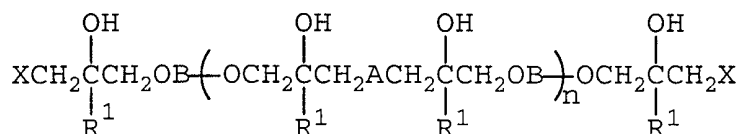
## THERMALLY STABLE POLYETHERAMINES

This invention relates to polyethers having pendant hydroxyl moieties and to methods of using them as barrier articles to protect oxygen-sensitive materials. More particularly, this invention relates to hydroxy-functionalized polyetheramines.

5 Hydroxy-functionalized polyetheramines are known and are described, for example, in U.S. Patents 5,275,853 and 5,464,924. These polyetheramines exhibit oxygen transmission rates of from 0.57 to 19 cm<sup>3</sup>-mil/100 in<sup>2</sup>-atm (O<sub>2</sub>)-day, and are useful in the fabrication of barrier containers and films and as molding, extrusion and casting resins.

10 Residual epoxy end groups in hydroxy-functionalized polyetheramines can sometimes limit their utility by promoting cross-linking and gelation during melt fabrication. Melt-stable hydroxy-functionalized polyetheramines, along with a process for their preparation, would clearly be desirable.

The present invention is, in a first aspect, a hydroxy-functionalized polyetheramine represented by the formula:



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wherein each A is independently an amine moiety and each B is independently a divalent aromatic moiety; R<sup>1</sup> is hydrogen or a hydrocarbyl moiety; X is (a) a monovalent moiety, which is not a secondary or tertiary amine and which does not contain a substituent capable of cross-linking the polyetheramine at normal processing temperature, or (b) a combination of (i) a monovalent moiety which is not a secondary or tertiary amine and which does not contain a substituent capable of cross-linking the polyetheramine at normal processing temperature and (ii) a monovalent moiety which is a secondary or tertiary amine; and n is a whole number from 5 to 1000.

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In a second aspect, the present invention is a process for preparing a hydroxy-functionalized polyetheramine which comprises reacting (1) a difunctional amine with (2) a diglycidyl ether or a diepoxy-functionalized poly(alkylene oxide) under conditions sufficient to cause the amine moieties to react with the epoxy moieties to form a polymer backbone having amine linkages, ether linkages and pendant hydroxyl moieties and then treating the reaction product with a monofunctional nucleophile which is not a primary or secondary amine, optionally in the presence of a catalyst.

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In a third aspect, the present invention is a laminate structure comprising one or more layers of an organic polymer and one or more layers of the hydroxy-functionalized polyetheramine of the first aspect, wherein the hydroxy-functionalized polyetheramine layer is adhered directly to a contiguous organic polymer layer without an adhesive layer

5 therebetween.

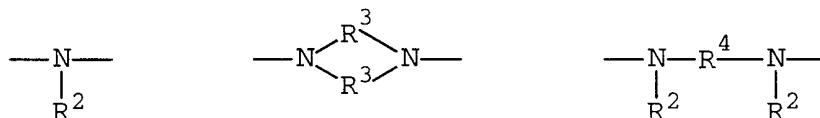
In a fourth aspect, the present invention is an article fabricated from the hydroxy-functionalized polyetheramine or laminate structure thereof, and can be in the form of a molded or coextruded container, or an impermeable monolayer or multilayer film. The article is suitable for packaging oxygen-sensitive materials such as foodstuffs and medicines.

10 In a fifth aspect, the present invention is a solvent or waterborne coating prepared from the hydroxy-functionalized polyetheramine.

These hydroxy-functionalized polyetheramines are melt stable thermoplastics and exhibit oxygen transmission rates below 20 cc-mil/100 in<sup>2</sup>-atm-day.

15 In addition to their use as barrier containers, films, laminate structures and coatings, the polymers of this invention are also useful as molding, extrusion and casting resins.

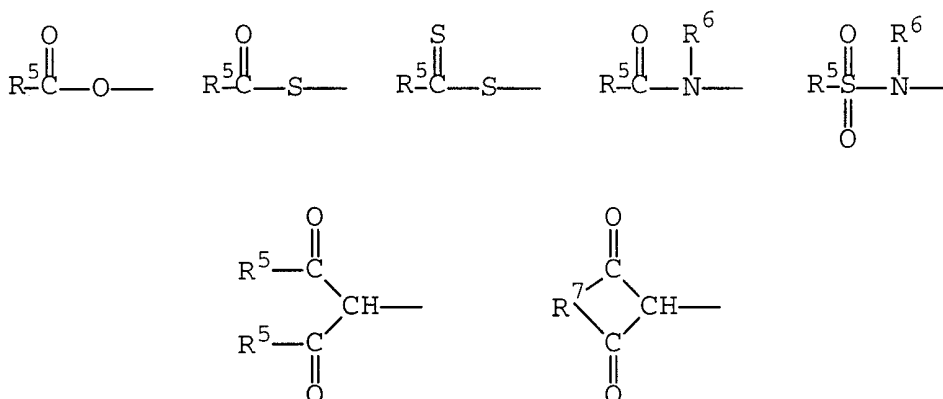
In preferred embodiments of the present invention, each A in the above formula is independently an amine moiety represented by any one of the formulas:



20 wherein R<sup>2</sup> is a hydrocarbyl, heterohydrocarbyl, intertly-substituted hydrocarbyl or intertly-substituted heterohydrocarbyl moiety, wherein the substituent(s) is hydroxyl, cyano, halo, arlyloxy, alkylamido, arylamido, alkylcarbonyl, or arylcarbonyl; R<sup>3</sup> and R<sup>4</sup> are independently a hydrocarbylene, heterohydrocarbylene, intertly-substituted hydrocarbylene or intertly-substituted heterohydrocarbylene moiety, wherein the substituent(s) is hydroxyl, cyano, halo, arlyloxy, alkylamido, arylamido, alkylcarbonyl, or arylcarbonyl with ethylene and p-xylylene being most preferred; each X is independently hydrogen, a primary amino moiety, a hydroxyl moiety, an alkyl, heteroalkyl, intertly-substituted alkyl or intertly-substituted heteroalkyl group, an aryl or intertly-substituted aryl group, an alkoxy or intertly-substituted alkoxy group; an arlyloxy or intertly-substituted arlyloxy group, an alkanethio or intertly-substituted alkanethio group; an arenethio or intertly-substituted arenethio group, wherein the substituent(s) is

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hydroxyl, cyano, halo, aryloxy, alkylamido, arylamido, alkylcarbonyl, or arylcarbonyl; or is represented by any one of the formulas:



- 5 wherein R<sup>5</sup> is independently an alkyl or heteroalkyl, intertly-substituted alkyl or heteroalkyl, aryl or intertly-substituted aryl group, wherein the substituent(s) is cyano, halo, aryloxy, alkylamido, arylamido, alkylcarbonyl, or arylcarbonyl; R<sup>6</sup> is independently hydrogen, an alkyl or heteroalkyl, intertly-substituted alkyl or heteroalkyl, aryl or intertly-substituted aryl group, wherein the substituent(s) is the same as that for R<sup>5</sup>; and R<sup>7</sup> is an alkylene or heteroalkylene,  
 10 intertly-substituted alkylene or heteroalkylene, arylene or intertly-substituted arylene moiety, wherein the substituent(s) is the same as that for R<sup>3</sup> and R<sup>4</sup>.

In the more preferred embodiments of the present invention, X is methoxy, ethoxy, propoxy, 2-(methoxy)ethoxy, 2-(ethoxy)ethoxy, benzyloxy, phenoxy, *p*-methylphenoxy, *p*-methoxyphenoxy, 4-*tert*-butylphenoxy, methylmercapto,  
 15 ethylmercapto, propylmercapto, 2-(methoxy)ethylmercapto, 2-(ethoxy)ethylmercapto, benzylmercapto, 2,3-dihydroxypropylmercapto, phenylmercapto, *p*-methylphenylmercapto, acetate, benzoate, acetamido or benzenesulfonamido; R<sup>1</sup> is hydrogen or methyl; R<sup>2</sup> is methyl, ethyl, propyl, isopropyl, 2-hydroxyethyl, 3-hydroxypropyl, 2-hydroxypropyl, 2,3-dihydroxypropyl, 2-(acetamido)ethyl, benzyl, phenyl, *p*-methoxyphenyl, *p*-methylphenyl;  
 20 R<sup>3</sup> is ethylene, 1,2-propylene or 1,2-butylene; and R<sup>4</sup> is ethylene, propylene, butylene, hexamethylene, 1,4-xylylene, 1,3-xylylene, 1,4-phenylene, 1,3-phenylene or 1,2-phenylene; and B is 1,4-phenylene, 1,3-phenylene, 1,2-phenylene, methylenediphenylene, isopropylidenediphenylene, oxydiphenylene, thiodiphenylene, carbonyldiphenylene, diphenylflourene or  $\alpha$ -methylstilbene or a combination thereof.

25 The hydroxy-functionalized polyetheramines of the present invention can be prepared by reacting a difunctional amine with an excess of a diglycidyl ether under conditions sufficient to cause the amine moieties to form a polymer backbone having amine

linkages, ether linkages and pendant hydroxyl moieties and then treating the reaction product with a monofunctional nucleophile which is not a primary or secondary amine, optionally in the presence of a catalyst. Alternatively, the hydroxy-functionalized polyetheramines can be prepared by reacting a difunctional amine with an equimolar amount of a diglycidyl ether and then treating the reaction product with a monofunctional nucleophile which is not a primary or secondary amine, optionally in the presence of a catalyst.

As used herein, the term "diglycidyl ether" means the reaction product of an aromatic, aliphatic or poly(alkylene oxide) diol with epichlorohydrin.

The difunctional amines which can be employed in the practice of the present invention include the bis-secondary amines and primary amines. Suitable bis-secondary amines include piperazine and substituted piperazines, for example dimethylpiperazine and 2-methylamidopiperazine; bis(N-methylamino)benzene, 1,2-bis(N-methylamino)ethane, and N,N'-bis(2-hydroxyethyl)ethylenediamine. Preferred bis-secondary amines are piperazine, dimethylpiperazine, and 1,2-bis(N-methylamino)ethane. The most preferred bis-secondary amine is piperazine. Suitable primary amines include aniline and substituted anilines, for example, 4-(methylamido)aniline, 4-methylaniline, 4-methoxyaniline, 4-*tert*-butylaniline, 3,4-dimethoxyaniline, 3,4-dimethylaniline; alkylamines, and substituted alkylamines, for example, butylamine and benzylamine; and alkanol amines; for example, 2-aminoethanol and 1-aminopropan-2-ol. Preferred primary amines are aniline, 4-methoxyaniline, 4-*tert*-butylaniline, butylamine, and 2-aminoethanol. Most preferred primary amines are 4-methoxyaniline and 2-aminoethanol.

The diglycidyl ethers which can be employed in the practice of the present invention for preparing the polyetheramines include the diglycidyl ethers of the amide-containing bisphenols such as N,N'-bis(hydroxyphenyl)alkylenedicarboxamides, N,N'-bis(hydroxyphenyl)arylenedicarboxamides, bis(hydroxybenzamido)alkanes or bis(hydroxybenzamido)arenes, N-(hydroxyphenyl)hydroxybenzamides, 2,2-bis(hydroxyphenyl)acetamides, N,N'-bis(3-hydroxyphenyl)glutaramide, N,N'-bis(3-hydroxyphenyl)adipamide, 1,2-bis(4-hydroxybenzamido) ethane, 1,3-bis(4-hydroxybenzamide)benzene, N-(4-hydroxyphenyl)-4-hydroxybenzamide, and 2,2-bis(4-hydroxyphenyl)acetamide, 9,9-bis(4-hydroxyphenyl) fluorene, hydroquinone, resorcinol, 4,4'-sulfonyl-diphenol, 4,4'-thiodiphenol, 4,4'-oxydiphenol, 4,4'-dihydroxybenzophenone, tetrabromoisopropylidene-bisphenol, dihydroxy dinitrofluorenylidenediphenylene, 4,4-bis(4-hydroxyphenyl)methane,  $\alpha,\alpha$ -bis(4-hydroxyphenyl)-ethylbenzene, 2,6-dihydroxynaphthalene and 4,4'-isopropylidene

bisphenol (bisphenol A). More preferred diglycidyl ethers are the diglycidyl ethers of 9,9-bis(4-hydroxyphenyl)fluorene, hydroquinone, resorcinol, 4,4'-sulfonyldiphenol, 4,4'-thiodiphenol, 4,4'-oxydiphenol, 4,4'-dihydroxybenzophenone, tetrabromoisopropylidenebisphenol, dihydroxy dinitrofluorenylidenediphenylene, 4,4'-biphenol, 4,4'-dihydroxybiphenylene oxide, bis(4-hydroxyphenyl)-methane,  $\alpha,\alpha$ -bis(4-hydroxyphenyl)ethylbenzene, 2,6-dihydroxynaphthalene and 4,4'-isopropylidene bisphenol (bisphenol A). Most preferred diglycidyl ethers are the diglycidyl ethers of 4,4'-isopropylidene bisphenol (bisphenol A), 4,4'-sulfonyldiphenol, 4,4'-oxydiphenol, 4,4'-dihydroxybenzophenone, and 9,9-bis(4-hydroxy-phenyl)fluorene.

10 The monofunctional nucleophiles which can be employed in the practice of the present invention include water, hydrogen sulfide, ammonia, ammonium hydroxide, a hydroxyarene, an aryloxide salt, a carboxylic acid, a carboxylic acid salt, a mercaptan or a thiolate salt. Preferably, the hydroxyarene is phenol, cresol, methoxyphenol, or 4-*tert*-butylphenol; the aryloxide salt is sodium or potassium phenate; the carboxylic acid is 15 acetic acid or benzoic acid; the carboxylic acid salt is sodium acetate, sodium benzoate, sodium ethylhexanoate, potassium acetate, potassium benzoate, potassium ethylhexanoate, or calcium ethylhexanoate; the mercaptan is 3-mercapto-1,2-propanediol or benzenethiol; and the thiolate salt is sodium or potassium benzenethiolate.

Preferred catalysts include metal hydroxides, quaternary ammonium salts or 20 quaternary phosphonium salts. Especially preferred catalysts include sodium hydroxide, potassium hydroxide, ammonium hydroxide, ethyltriphenylphosphonium acetate, tetrabutylammonium bromide and bis(triphenylphosphoranylidene)ammonium chloride.

The conditions at which the reaction is most advantageously conducted are dependent on a variety of factors, including the specific reactants, solvent, and catalyst 25 employed but, in general, the reaction is conducted under a non-oxidizing atmosphere such as a blanket of nitrogen, preferably at a temperature from 100°C to 190°C. The reaction can be conducted neat (without solvent or other diluents). However, in order to ensure homogeneous reaction mixtures at such temperatures, it is often desirable to use inert organic solvents for the reactants. Examples of suitable solvents include 30 1-methyl-2-pyrrolidinone (NMP), and ethers or hydroxy ethers such as diglyme, triglyme, diethylene glycol ethyl ether, diethylene glycol methyl ether, dipropylene glycol methyl ether, propylene glycol phenyl ether, propylene glycol methyl ether and tripropylene glycol methyl ether.

After treating the reaction product with a monofunctional nucleophile which is not a primary or secondary amine, the polyetheramine can be recovered from the reaction mixture by conventional methods. For example, the reaction mixture containing the polymer can be diluted with a suitable solvent such as dimethylformamide, cooled to room  
5 temperature, and the polymer isolated by precipitation from a non-solvent such as a 50/50 mixture of methanol and water. The precipitated polymer can then be purified by washing such as by a first wash with fresh 50/50 mixture of methanol and water and then fresh water. The polymer is collected by filtration, washed with a suitable solvent, such as water and then dried.

10 Films prepared from the hydroxy-functionalized polyetheramine of the present invention generally have oxygen transmission rates (OTR) from 0.1 to 4 cc-mil/100 in<sup>2</sup>/atm/day, at 25°C and 60 percent relative humidity (ASTM D-3985); carbon dioxide transmission rates (CO<sub>2</sub>TR) from 1.5 to 35 cc-mil/100 in<sup>2</sup>-atm-day, at 23°C and 0 percent relative humidity and water vapor transmission rates (WVTR) from 0.7 to 3.5 cc-mil/100 in<sup>2</sup>-  
15 atm-day, at 38°C and 90 percent relative humidity (ASTM F-372).

Films and laminate structures can be formed from the hydroxy-functionalized polyetheramine of the present invention by using conventional extrusion techniques such as feedblock extrusion, multimanifold die coextrusion or combinations of the two, or by solvent spraying or solution casting. Solution casting is a well known process and is described, for  
20 example, in the *Plastics Engineering Handbook* of the Society of the Plastics Industry, Inc, 4th Edition, page 448.

Containers and other molded parts can be fabricated from the films or laminate structures comprising the hydroxy-functionalized polyetheramine of the present invention by using conventional fabricating techniques for thermoplastic polymers such as  
25 compression molding, injection molding, extrusion, thermoforming, blow molding and solvent casting.

In general, laminate structures can be formed from the hydroxy-functionalized polyetheramine of the present invention by coextruding one or more layers of an organic polymer and one or more layers of the hydroxy-functionalized polyetheramine, wherein the  
30 hydroxy-functionalized polyetheramine layer is adhered directly to a contiguous organic polymer layer without an adhesive layer therebetween.

The laminate structure can be a three-layer laminate comprising a first outer layer of an organic polymer, a core layer of the hydroxy-functionalized polyetheramine and a



second outer layer of an organic polymer which is the same as or different from the organic polymer of the first outer layer.

The laminate structure can also be a three-layer laminate comprising a first outer layer of the hydroxy-functionalized polyetheramine, a core layer of an organic polymer  
5 and a second outer layer of an organic polymer which is the same as or different from the organic polymer of the core layer.

The laminate structure can also be a three-layer laminate comprising a first outer layer of the hydroxy-functionalized polyetheramine, a core layer of an organic polymer  
10 and a second outer layer of the hydroxy-functionalized polyetheramine which is the same as or different from the hydroxy-functionalized polyetheramine of the first outer layer.

Organic polymers which can be employed in the practice of the present invention for preparing the laminate structure include crystalline thermoplastic polyesters, such as polyethylene terephthalate (PET); polyamides, polyolefins, and polyolefins based on monovinyl aromatic monomers.

15 Polyesters and methods for their preparation are well known in the art and reference is made thereto for the purposes of this invention. For purposes of illustration and not limitation, reference is particularly made to pages 1-62 of Volume 12 of the *Encyclopedia of Polymer Science and Engineering*, 1988 revision, John Wiley & Sons.

20 Polyamides which can be employed in the practice of the present invention include the various grades of nylon, such as nylon 6, nylon 66 and nylon 12.

Polyolefins which can be employed in the practice of the present invention include, for example, low density polyethylene, linear low density polyethylene, very low density polyethylene, polypropylene, polybutene, ethylene/vinyl acetate copolymers, ethylene/propylene copolymers and ethylene/butene-1 copolymers.

25 Polyolefins based on monovinyl aromatic monomers which can be employed in the practice of the present invention include polystyrene, polymethylstyrene, styrene/methylstyrene or styrene/chlorostyrene copolymers.

30 Other organic polymers of the polyester or polyamide type can also be employed in the practice of the present invention for preparing the laminate structure. Such polymers include polyhexamethylene adipamide, polycaprolactone, polyhexamethylene sebacamide, polyethylene 2,6-naphthalate and polyethylene 1,5-naphthalate, polytetramethylene 1,2-dioxybenzoate and copolymers of ethylene terephthalate and

ethylene isophthalate.

The thickness of each layer in the laminate structure is dependent on a number of factors, including the intended use, materials stored in the container, the length of storage prior to use and the specific composition employed in each layer of the laminate.

5 In general, the laminate structure will have a total thickness of from 0.5 to 500 mils, preferably from 1.0 to 250 mils; with the thickness of the hydroxy-functionalized polyetheramine layer(s) being from 0.05 to 100 mils, preferably from 0.1 to 50 mils; and the thickness of the polyester layer(s) being from 0.45 to 400 mils, preferably from 0.9 to 200 mils.

10 The hydroxy-functionalized polyetheramine can also be prepared and fabricated into a shaped article by a reactive extrusion process wherein the reactants are fed into and reacted in an extruder using the conditions described in U.S. Patent No. 4,612,156, which is.

The following working examples are given to illustrate the invention and should not be construed as limiting its scope. Unless otherwise indicated, all parts and percentages are by weight.

### Examples

#### Comparative Example A

20 A stirred solution of the diglycidyl ether of bisphenol A (epoxy equivalent weight = 172.3; 212.56 g, 0.617 mol), ethanolamine (37.44 g, 0.614 mol) and dipropylene glycol methyl ether (170 mL) was heated slowly to 152°C and then maintained at 140°C to 143°C for 1.5 hours, during which 20 to 50 mL aliquots of additional solvent (330 mL) were added to ensure adequate stirring as the solution viscosity increased. The solution was allowed to cool to room temperature and then poured into a vigorously stirred solution of 25 methanol (300 mL) and ice water (2.2 L) to precipitate a polyetheramine as fibrous powder, which was collected by decantation, stirred with methanol/water and collected by filtration. The product then was mechanically agitated with 4:1 water/methanol for 24 hours, collected by filtration, dried *in vacuo* at 35°C for 4 hours, redissolved in tetrahydrofuran (2 mL/gram of product), again precipitated from methanol/water and dried *in vacuo* at 82°C for 16 hours, 30 after which the polymer was no longer soluble in tetrahydrofuran or dimethylformamide (DMF). These results indicate that the polymer cross-links at elevated temperature and is not thermoplastic.

Example 1

A stirred 85.7 g solution of polyetheramine (29.5 g) in dipropylene glycol methyl ether, prepared as described in Comparative Example A prior to product precipitation and isolation, was heated to 52°C, charged with 0.91 g of ammonium hydroxide solution (28 to 30 percent aqueous ammonia), and then maintained at 71°C for 18 hours. Additional aqueous ammonia (0.65 g) was then added and stirring at 143°C was continued for 1.5 hours. The product was then isolated as described in Comparative Example A. After drying *in vacuo* at 76°C for 16 hours, the product remained soluble in DMF, has an inherent viscosity of 0.64 dL/g (0.5 g/dL; DMF; 25°C), and showed essentially no change in an initial melt viscosity of about 1000 Pa • s after 30 minutes at 200°C as measured with a rheometer in oscillatory mode at 5 percent strain and 10 rad/s at a gap distance of 0.5 mm. These results showed that ammonia consumed any residual epoxy groups in the product, and yielded a thermally processible thermoplastic.

Example 2

A stirred 98.7 g solution of polyetheramine (34.0 g) in dipropylene glycol methyl ether, prepared as described in Comparative Example A prior to product precipitation and isolation, was charged with benzoic acid (2.0 g), and then maintained at 134°C to 143°C for 2 hours. The product was then isolated as described in Comparative Example A. After drying *in vacuo* at 82°C for 16 hours, the product remained soluble in DMF, had an inherent viscosity of 0.68 dL/g (0.5 g/dL; DMF; 25°C), and showed essentially no change in an initial melt viscosity of about 1000 Pa • s after 30 minutes at 200°C as measured with a rheometer in oscillatory mode at 5 percent strain and 10 rad/s at a gap distance of 0.5 mm. These results showed that ammonia consumed any residual epoxy groups in the product and yielded a thermally processible thermoplastic.

Example 3

A stirred 98.1 g solution of polyetheramine (33.8 g) in dipropylene glycol methyl ether, prepared as described in Comparative Example A prior to product precipitation and isolation, was charged with phenol (1.52 g), and heated to 80°C, after which 0.11 g of tetrabutylphosphonium acetate (50 percent in methanol) was added, and the resulting solution was maintained at 150°C for 2.5 hours. The product was then isolated as described in Comparative Example A. After drying *in vacuo* at 82°C for 16 hours, the product remained soluble in DMF, had an inherent viscosity of 0.55 dL/g (0.5 g/dL; DMF; 25°C), and showed

essentially no change in an initial melt viscosity of about 1000 Pa • s after 30 minutes at 200°C as measured with a rheometer in oscillatory mode at 5 percent strain and 10 rad/s at a gap distance of 0.5 mm. These results showed that ammonia consumed any residual epoxy groups in the product and yielded a thermally processible thermoplastic.

#### 5 Example 4

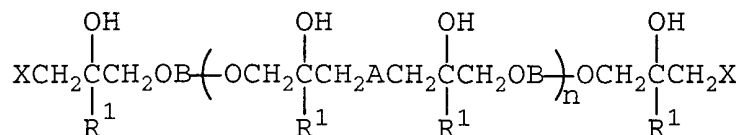
A stirred 98.8 g solution of polyetheramine (34.0 g) in dipropylene glycol methyl ether, prepared as described in Comparative Example A prior to product precipitation and isolation, was charged with 3-mercapto-1,2-propanediol (2.0 g), and then maintained at 81°C for 12 hours and then at 149°C for 3 hours. The product was then isolated as  
10 described in Comparative Example A. After drying *in vacuo* at 82°C for 16 hours, the product remained soluble in DMF, had an inherent viscosity of 0.46 dL/g (0.5 g/dL; DMF; 25°C), and showed essentially no change in an initial melt viscosity of about 1000 Pa • s after  
30 minutes at 200°C as measured with a rheometer in oscillatory mode at 5 percent strain and 10 rad/s at a gap distance of 0.5 mm. These results showed that ammonia consumed  
15 any residual epoxy groups in the product and yielded a thermally processible thermoplastic.

#### Example 5

A stirred 111.5 g solution of polyetheramine (38.4 g) in dipropylene glycol methyl ether, prepared as described in Comparative Example A prior to product precipitation and isolation, was charged with 4-*tert*-butylphenol (2.76 g) and heated to 80°C.  
20 Tetrabutylphosphonium acetate (50 percent in methanol, 0.086 g) was added and the solution was stirred at 149°C for 3 hours. The product was then isolated as described in Comparative Example A. After drying *in vacuo* at 82°C for 16 hours, the product remained soluble in DMF, had an inherent viscosity of 0.62 dL/g (0.5 g/dL; DMF; 25°C), and shows essentially no change in an initial melt viscosity of about 1000 Pa • s after 30 minutes at  
25 200°C as measured with a rheometer in oscillatory mode at 5 percent strain and 10 rad/s at a gap distance of 0.5 mm. These results show that ammonia consumes any residual epoxy groups in the product and yields a thermally processible thermoplastic.

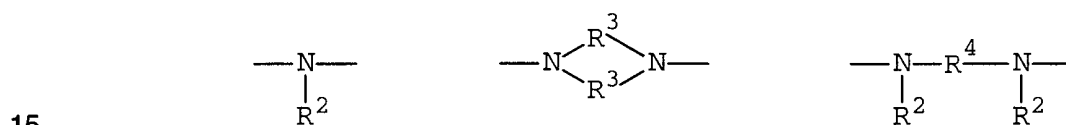
CLAIMS:

1. A thermoplastic hydroxy-functionalized polyetheramine having the formula:



5 wherein each A is independently an amine moiety and each B is independently a divalent aromatic moiety; R<sup>1</sup> is hydrogen or a hydrocarbyl moiety; each X is independently (a) a monovalent moiety, which is not a secondary or tertiary amine and which does not contain a substituent capable of cross-linking the polyetheramine at normal processing temperature; or  
 10 (b) a combination of (i) a monovalent moiety which is not a secondary or tertiary amine and which does not contain a substituent capable of cross-linking the polyetheramine at normal processing temperature and (ii) a monovalent moiety which is a secondary or tertiary amine; and n is a whole number from 5 to 1000.

2. The polyetheramine of Claim 1 wherein A in the formula is represented by any one of the formulas:

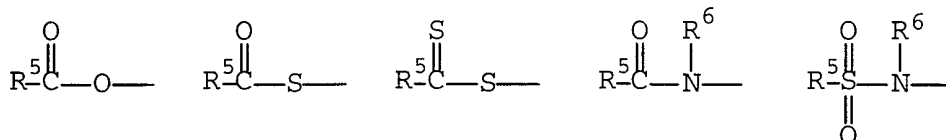


wherein each R<sup>2</sup> is independently a hydrocarbyl, heterohydrocarbyl, intertly-substituted hydrocarbyl or intertly-substituted heterohydrocarbyl moiety, wherein the substituent(s) is hydroxyl, cyano, halo, arlyloxy, alkylamido, arylamido, alkylcarbonyl, or arylcarbonyl; R<sup>3</sup> and R<sup>4</sup> are independently a hydrocarbylene, heterohydrocarbylene, intertly-substituted  
 20 hydrocarbylene or intertly-substituted heterohydrocarbylene moiety, wherein the substituent(s) is alkylamido, hydroxy, alkoxy, halo, cyano, arlyloxy, alkylcarbonyl or arylcarbonyl.

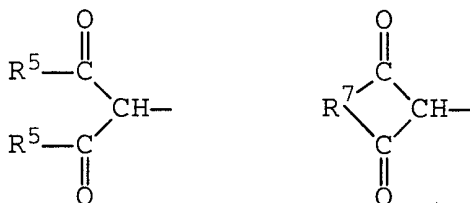
3. The polyetheramine of Claim 2 wherein each X is independently hydrogen, a primary amino moiety, a hydroxyl moiety, an alkyl, heteroalkyl, intertly-  
 25 substituted alkyl or intertly-substituted heteroalkyl group, an aryl or intertly-substituted aryl group; an alkoxy or intertly-substituted alkoxy group; an arlyloxy or intertly-substituted arlyloxy group; an alkanethio or intertly-substituted alkanethio group; an arenethio or intertly-

substituted arenethio group; wherein the substituent(s) is hydroxyl, cyano, halo, aryloxy, alkylamido, arylamido, alkylcarbonyl, or arylcarbonyl.

4. The polyetheramine of Claim 2 wherein each X is independently represented by any one of the formulas:



5



- wherein  $\text{R}^5$  is independently an alkyl or heteroalkyl, intertly-substituted alkyl or heteroalkyl, aryl or intertly-substituted aryl group, wherein the substituent(s) is cyano, halo, aryloxy, alkylamido, arylamido, alkylcarbonyl, or arylcarbonyl;  $\text{R}^6$  is independently hydrogen, an alkyl or heteroalkyl, intertly-substituted alkyl or heteroalkyl, aryl or intertly-substituted aryl group, wherein the substituent(s) is the same as that for  $\text{R}^5$ ; and  $\text{R}^7$  is an alkylene or heteroalkylene, intertly-substituted alkylene or heteroalkylene, arylene or intertly-substituted arylene moiety, wherein the substituent(s) is the same as that for  $\text{R}^3$  and  $\text{R}^4$ .

5. The polyetheramine of Claim 2 wherein X is methoxy, ethoxy, propoxy, 2-(methoxy)ethoxy, 2-(ethoxy)ethoxy, benzyloxy, phenyloxy, *p*-methylphenyloxy, *p*-methoxyphenoxy, 4-*tert*-butylphenyloxy, methylmercapto, ethylmercapto, propylmercapto, 2-(methoxy)ethylmercapto, 2-(ethoxy)ethylmercapto, benzylmercapto, 2,3-dihydroxypropylmercapto, phenylmercapto, *p*-methylphenylmercapto, acetate, benzoate, acetamido or benzenesulfonamido.

6. The polyetheramine of Claim 2 wherein  $\text{R}^1$  is hydrogen or methyl;  $\text{R}^2$  is methyl, ethyl, propyl, isopropyl, 2-hydroxyethyl, 3-hydroxypropyl, 2-hydroxypropyl, 2,3-dihydroxypropyl, 2-(acetamido)ethyl, benzyl, phenyl, *p*-methoxyphenyl, *p*-methylphenyl;  $\text{R}^3$  is ethylene, 1,2-propylene or 1,2-butylene; and  $\text{R}^4$  is ethylene, 1,2-propylene or 1,2-butylene, propylene, butylene, hexamethylene, 1,4-xylylene, 1,3-xylylene, 1,4-phenylene, 1,3-phenylene or 1,2-phenylene.

7. The polyetheramine of Claim 6 wherein B is 1,4-phenylene, 1,3-phenylene, 1,2-phenylene, methylenediphenylene, isopropylidenediphenylene, oxydiphenylene, thiodiphenylene, carbonyldiphenylene, diphenylflourene or  $\alpha$ -methylstilbene or a combination thereof.

5 8. The polyetheramine of Claim 1 which is the reaction product of a diglycidyl ether, a difunctional amine and a monofunctional nucleophile which is not a primary or secondary amine.

9. A process for preparing a thermoplastic hydroxy-functionalized polyetheramine which comprises reacting a difunctional amine with an excess or an  
10 equimolar amount of a diglycidyl ether, and treating the reaction product with a monofunctional nucleophile which is not a primary or secondary amine, optionally in the presence of a catalyst.

10. The process of Claim 9 wherein the monofunctional nucleophile is water, hydrogen sulfide, ammonia, ammonium hydroxide, a hydroxyarene, an aryloxide salt,  
15 a carboxylic acid, a carboxylic acid salt, a mercaptan, or thiolate salt.

11. The process of Claim 10 wherein the hydroxyarene is phenol, cresol, methoxyphenol, or 4-*tert*-butylphenol.

12. The process of Claim 10 wherein the aryloxide salt is sodium or potassium phenate.

20 13. The process of Claim 10 wherein the carboxylic acid is acetic acid or benzoic acid.

14. The process of Claim 10 wherein the carboxylic acid salt is sodium acetate, sodium benzoate, sodium ethylhexanoate, potassium acetate, potassium benzoate, potassium ethylhexanoate, or calcium ethylhexanoate.

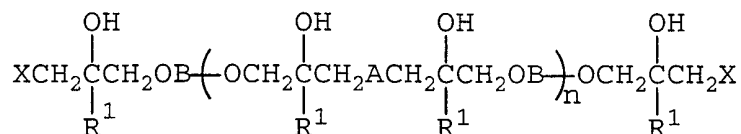
25 15. The process of Claim 10 wherein the mercaptan is 3-mercapto-1,2-propanediol or benzenethiol.

16. The process of Claim 10 wherein the thiolate salt is sodium or potassium benzenethiolate.

17. The process of Claim 9 wherein the catalyst is a quaternary ammonium salt, a quaternary phosphonium salt or a metal hydroxide.

18. The process of Claim 9 wherein the catalyst is ammonium hydroxide, ethyltriphenylphosphonium acetate, tetrabutylammonium bromide,  
 5 bis(triphenylphosphoranylidene)ammonium chloride, sodium hydroxide or potassium hydroxide.

19. A laminate structure comprising one or more layers of an organic polymer and one or more layers of a hydroxy-functionalized polyetheramine, wherein said hydroxy-functionalized polyetheramine layer is adhered directly to a contiguous organic  
 10 polymer layer without an adhesive layer therebetween, the hydroxy-functionalized polyetheramine having the formula:



wherein each A is independently an amine moiety and each B is independently a divalent aromatic moiety; R<sup>1</sup> is hydrogen or a hydrocarbyl moiety; each X is independently (a) a  
 15 monovalent moiety, which is not a secondary or tertiary amine and which does not contain a substituent capable of cross-linking the polyetheramine at normal processing temperature, or (b) a combination of (i) a monovalent moiety which is not a secondary or tertiary amine and which does not contain a substituent capable of cross-linking the polyetheramine at normal processing temperature and (ii) a monovalent moiety which is a secondary or tertiary amine,  
 20 and n is a whole number from 5 to 1000.

20. The laminate structure of Claim 19 comprising outer layers of an organic polymer and a core layer of the hydroxy-functionalized polyetheramine.

21. The laminate structure of Claim 19 comprising a first outer layer of the hydroxy-functionalized polyetheramine, a core layer of an organic polymer and a second  
 25 outer layer of an organic polymer which is the same as or different from the organic polymer of the core layer.

22. The laminate structure of Claim 19 comprising a first outer layer of the hydroxy-functionalized polyetheramine, a core layer of an organic polymer and a second



outer layer of the hydroxy-functionalized polyetheramine, which is the same as or different from the hydroxy-functionalized polyetheramine of the first outer layer.

23. The laminate structure of Claim 19 wherein the organic polymer is a crystalline thermoplastic polyester, a polyamide, a polyolefin or a polyolefin based on monovinyl aromatic monomers.
24. The laminate structure of Claim 23 wherein the crystalline polyester is polyethyleneterephthalate.
25. The laminate structure of Claim 23 wherein the polyamide is nylon 6, nylon 66 or nylon 12.
26. The laminate structure of Claim 23 wherein the polyolefin is polyethylene and the polyolefin based on monovinyl aromatic monomers is polystyrene, polymethylstyrene, styrene/methylstyrene copolymer or styrene/chlorostyrene copolymer.
27. The laminate structure of Claim 23 wherein the organic polymer is polyhexamethylene adipamide, polycaprolactone, polyhexamethylene sebacamide, polyethylene 2,6-naphthalate, polyethylene 1,5-naphthalate, polytetramethylene 1,2-dioxybenzoate or ethylene terephthalate/ethylene isophthalate copolymer.
28. The polyetheramine of Claim 1 in the form of a barrier film, a barrier container, a barrier coating, a foam or a molded article.
29. A solvent or waterborne coating composition prepared from the hydroxy-functionalized polyetheramine of Claim 1.

# INTERNATIONAL SEARCH REPORT

Internal Application No

PCT/US 98/21554

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC 6 C08G59/18 C08G59/50 B32B27/08

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 6 C08G B32B

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)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 464 924 A (SILVIS H CRAIG ET AL) 7 November 1995 cited in the application see column 3, line 55-57 see column 5, line 47 - column 6, line 2 ---	1-29
X	US 5 686 551 A (WHITE JERRY E ET AL) 11 November 1997 see column 5, line 54 - line 61 ---	1-29
A	US 5 275 853 A (SILVIS H CRAIG ET AL) 4 January 1994 cited in the application see column 4, line 34 - line 59 --- -/--	1-29

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

° Special categories of cited documents :

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- "O" document referring to an oral disclosure, use, exhibition or other means
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Date of the actual completion of the international search

18 February 1999

Date of mailing of the international search report

02/03/1999

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# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/21554

**C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT**

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 96 18669 A (PPG INDUSTRIES INC) 20 June 1996 see page 10, line 8 - line 22 see page 14, line 14 - line 26 ---	1-29
A	EP 0 253 405 A (DOW CHEMICAL CO) 20 January 1988 see page 8, line 25 - page 10, line 50 ---	1-18
A	EP 0 327 039 A (PPG INDUSTRIES INC) 9 August 1989 -----	1-29

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/21554

Patent document cited in search report	A	Publication date	Patent family member(s)	Publication date
US 5464924	A	07-11-1995	NONE	
<hr style="border-top: 1px dashed black;"/>				
US 5686551	A	11-11-1997	NONE	
<hr style="border-top: 1px dashed black;"/>				
US 5275853	A	04-01-1994	AT 163949 T	15-03-1998
			AU 642303 B	14-10-1993
			AU 8553691 A	09-04-1992
			CA 2052653 A	04-04-1992
			DE 69129055 D	16-04-1998
			DE 69129055 T	06-08-1998
			EP 0479445 A	08-04-1992
			ES 2113366 T	01-05-1998
			FI 914619 A	04-04-1992
			JP 4272926 A	29-09-1992
			NZ 240001 A	23-12-1993
<hr style="border-top: 1px dashed black;"/>				
WO 9618669	A	20-06-1996	AU 3679995 A	03-07-1996
			CA 2206898 A	20-06-1996
			EP 0797608 A	01-10-1997
			US 5637365 A	10-06-1997
<hr style="border-top: 1px dashed black;"/>				
EP 0253405	A	20-01-1988	US 4868230 A	19-09-1989
			US 4698141 A	06-10-1987
			AU 599681 B	26-07-1990
			AU 7575787 A	21-01-1988
			CA 1325858 A	04-01-1994
			CN 1016430 B	29-04-1992
			CN 1052320 A	19-06-1991
			DE 3786959 A	16-09-1993
			DE 3786959 T	03-02-1994
			DK 376287 A	19-01-1988
			ES 2058079 T	01-11-1994
			JP 1922766 C	07-04-1995
			JP 6047611 B	22-06-1994
			JP 63092637 A	23-04-1988
			WO 8800600 A	28-01-1988
			US 4980397 A	25-12-1990
			US 4977202 A	11-12-1990
			CA 1325070 A	07-12-1993
<hr style="border-top: 1px dashed black;"/>				
EP 0327039	A	09-08-1989	CA 1337137 A	26-09-1995
			DE 68928668 D	18-06-1998
			DE 68928668 T	26-11-1998
			ES 2116261 T	16-07-1998
			JP 2004820 A	09-01-1990
			JP 2057215 C	23-05-1996
			JP 7091368 B	04-10-1995
			MX 166278 B	28-12-1992
			MX 9205371 A	31-03-1994
			US 5489455 A	06-02-1996
			US 5438109 A	01-08-1995
			US 5008137 A	16-04-1991
			US 5491204 A	13-02-1996
			US 5573819 A	12-11-1996
			US 5300541 A	05-04-1994