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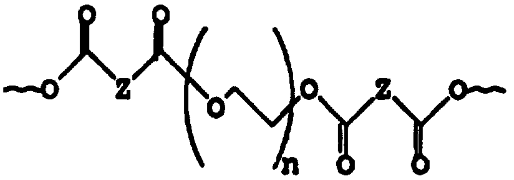
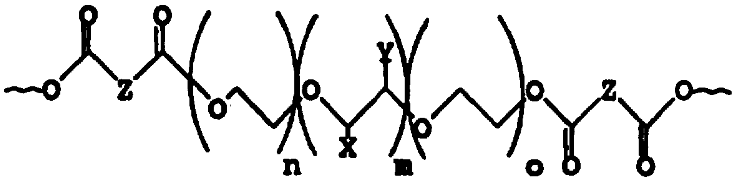
(54) Title: EPOXY-FUNCTIONAL POLYETHERS

(57) Abstract

A novel epoxy-functional polyether composition is produced by reacting (a) a carboxylic acid having formula (VI): H-Q-H, wherein Q is A or B, Z is a hydrocarbylene moiety, X and Y are independently a hydrogen, methyl or ethyl group with the provision that if X is methyl or ethyl, Y is hydrogen or if Y is methyl or ethyl, X is hydrogen, and n+m+o is a positive real number from 1 to 450 and (b) an epoxy resin having a functionality of at least 1.5 epoxide group per molecule.



(a)



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EPOXY-FUNCTIONAL POLYETHERS

The invention relates to epoxy-functional polyethers.

There are ever increasing demands for compounds useful in epoxy resin applications, for example as emulsifiers or diluents, as epoxy resins are required to perform under ever more specific and demanding conditions. In this respect reference is especially made to aqueous based epoxy resin compositions which are more environment-friendly than the classic organic solvent based systems. Such aqueous based systems require specific emulsifiers and/or diluents which have to be compatible with the aqueous phase as well as with the organic phase. It is desirable for such compounds to have epoxy functional groups to increase the compatibility with the cured epoxy matrix. Further, it is desirable to be able to provide compounds with predefined hydrophilic and hydrophobic segments depending on the desired applications.

It is an object of the present invention to provide compositions comprising novel epoxy-functional polyethers. It is another object of the present invention to provide a process to prepare epoxy-functional polyethers. Another object of the invention are the novel esters themselves.

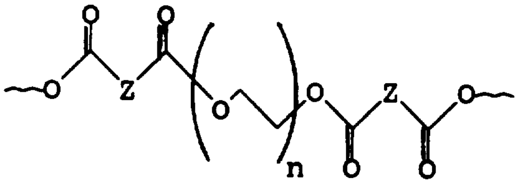
It has been found that compositions comprising certain epoxy-functional polyethers can be made, which polyethers are very suitable for use as emulsifier and/or reactive diluent in e.g. aqueous epoxy resin compositions which are suitable for coating purposes, by reaction of certain dicarboxylic acids and epoxy resins having more than one epoxy group.

Thus, the present invention relates to compositions comprising a product produced by reacting (a) a carboxylic acid having the formula:

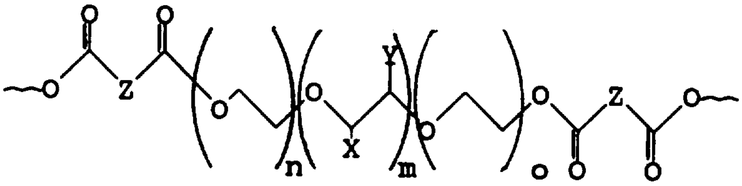
H-Q-H

(VI)

A =

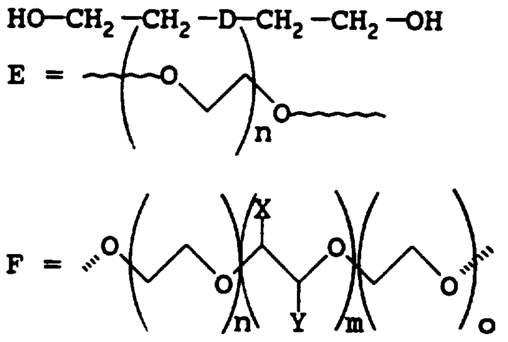


B =



wherein Q is A or B, Z is a C_{1-20} hydrocarbylene moiety, X and Y are independently a hydrogen, methyl or ethyl group with the provision that if X is methyl or ethyl, Y is hydrogen or if Y is methyl or ethyl, X is hydrogen, and n+m+o is a positive real number from 1 to 450 and (b) an epoxy resin having a functionality of at least 1.5 epoxide group per molecule in a carboxylic acid to epoxy resin mole ratio of from 1:2 to 1:20.

The hydrophilic carboxylic acid can be produced by reacting a polyethylene glycol, polypropylene glycol, polybutylene glycol or a block copolymer of ethylene oxide and propylene oxide or polybutylene oxide ("polyalkylene glycol") with an anhydride. Preferably the polyalkylene glycol has a formula:



(VII)

wherein D is E or F, X and Y are independently hydrogen, methyl or ethyl groups with the provision that if X is methyl or ethyl, Y is hydrogen or if Y is methyl or ethyl, X is hydrogen and m+n+o is a positive real number from 1, preferably from 20 to 450, preferably to 400 and m, n and o can independently be a positive real number from 0 to 450.

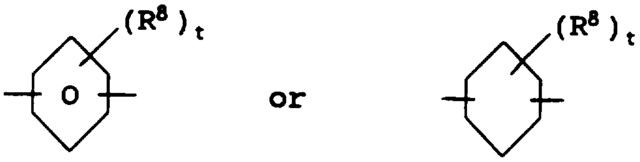
Polyalkylene glycols generally contain a distribution of compounds with a varying number of oxyethylene units, n or o and/or oxypropylene or oxybutylene units, m. Generally, the quoted number of units is the whole number closest to the statistical average, and the peak of the distribution. Positive real number as used herein refers to a number which is positive and includes integers and fractions of integers.

The carboxylic acids can be produced by reacting the polyalkylene glycols with a cyclic anhydride to prepare the corresponding diacids. Preferable cyclic anhydrides include, for example, methylhexahydrophthalic anhydride, ethylhexahydrophthalic anhydride, phthalic anhydride, tetrahydrophthalic anhydride, succinic anhydride, maleic anhydride, bicyclo[2.2.1]heptane, 2,3-dicarboxylic anhydride and chlorendic anhydride. The mole ratio of the polyalkylene glycol to anhydride is within the range of about 1:2 to about 1:1.8, preferably in an equivalent amount. When determining the mole ratio or equivalency of the polyalkylene glycol and the anhydride, the hydroxyl group in the polyalkylene glycol is counted as 2 and the carboxylic acid groups in the anhydride are counted as 1.

The carboxylic acid can be represented by the general formula:

$$H\text{-}Q\text{-}H \qquad \text{(VI)}$$

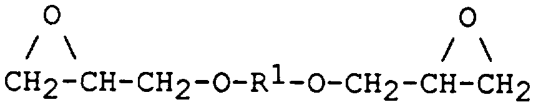
wherein Q, X, Y and Z are defined above. Preferably Z is C_{1-20} alkylene, C_{3-20} cycloalkylene which includes bicyclic moieties, C_{4-20} alkylene substituted cycloalkylene, C_{6-20} arylene, or C_{7-20} alkyl substituted arylene. More preferably Z is C_{1-20} alkylene, C_{5-6} cycloalkylene, C_{6-12} arylene, C_{7-20} alkylene substituted cycloalkylene or C_{7-20} alkyl substituted arylene. In a most preferred embodiment Z corresponds to



wherein R^8 is C_{1-10} alkyl, and t is 0 or 1. Preferably R^8 is C_{1-3} alkyl, and most preferably methyl.

The epoxy-functional polyethers of the invention are produced by reacting the carboxylic acid described above with a hydrophobic epoxy resin. Generally, the epoxy resin can be any reactive epoxy resin having a 1,2-epoxy equivalency (functionality) preferably, on the average, greater than 1.5 epoxide groups per molecule. The epoxy resin can be saturated or unsaturated, linear or branched, aliphatic, cycloaliphatic, aromatic or heterocyclic, and may bear substituents which do not materially interfere with the reaction with the carboxylic acid. Such substituents can include bromine or fluorine. They may be monomeric or polymeric, liquid or solid, but are preferably liquid or a low melting solid at room temperature. Suitable epoxy resins include glycidyl ethers prepared by reacting epichlorohydrin with a compound containing a real positive number of at least 1.5 aromatic hydroxyl group carried out under alkaline reaction conditions. Examples of epoxy resins suitable for use in the invention include diglycidyl ethers of dihydric compounds. Generally epoxy resins contain a distribution of compounds with a varying number of 1,2-epoxy equivalency.

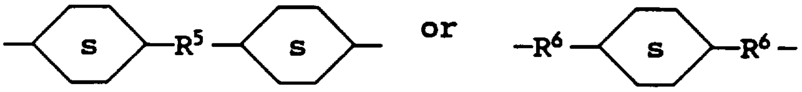
Preferred epoxy resins include, but are not limited to those represented by the formula:



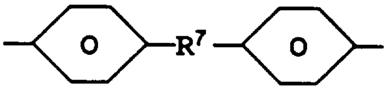
$$\overset{O}{\overbrace{CH_2-CH}}-CH_2-O-R^1-O-CH_2-\overset{O}{\overbrace{CH-CH_2}}$$

(VIII)

wherein R^1 is divalent aliphatic, divalent cycloaliphatic, divalent aryl or divalent arylaliphatic group, preferably R^1 contains about 8 to 120 carbon atoms. The term divalent aliphatic group includes compounds having oxygen atoms and/or sulphur atoms on the backbone. For example, R^1 can be a divalent cylcoaliphatic group having the formula



wherein R^5 and R^6 are each independently an alkylene group or a divalent arylaliphatic group having the formula



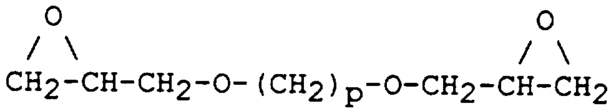
wherein R^7 is an alkylene group.

Preferably the epoxy resin is a diglycidyl ether of a dihydric phenol, diglycidyl ether of a hydrogenated dihydric phenol (cycloaliphatic glycidyl ether), an aliphatic glycidyl ether or cycloaliphatic epoxies.

Diglycidyl ethers of dihydric phenols can be produced, for example, by reacting an epihalohydrin with a dihydric phenol in the presence of an alkali. Examples of suitable dihydric phenols include: 2,2-bis(4-hydroxyphenyl) propane (bisphenol-A); 2,2-bis(4-hydroxy-3-tert-butylphenyl) propane; 1,1-bis-(4-hydroxyphenyl) ethane; 1,1-bis(4-hydroxyphenyl) isobutane; bis(2-hydroxy-1-naphthyl) methane; 1,5-dihydroxynaphthalene; 1,1-bis(4-hydroxy-3-alkylphenyl) ethane and the like. Suitable dihydric phenols can also be obtained from the reaction of phenol with aldehydes such as formaldehyde (bisphenol-F). Diglycidyl ethers of dihydric phenols includes fusion products of the above diglycidyl ethers of dihydric phenols with phenolic compounds such as bisphenol-A, such as those described in U.S. Patent Nos. 3,477,990 and 4,734,468.

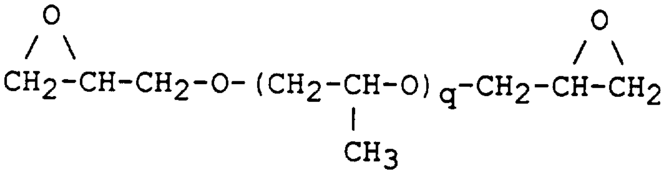
Diglycidyl ethers of hydrogenated dihydric phenols (or cycloaliphatic glycidyl ethers) can be produced, for example, by hydrogenation of dihydric phenols followed by glycidation with epihalohydrin in the presence of a Lewis acid catalyst and subsequent formation of the glycidyl ether by reaction with sodium hydroxide. Examples of suitable dihydric phenols are listed above.

Aliphatic glycidyl ethers optionally containing oxygen atoms on the backbone in the form of ether linkages can be produced, for example, by reacting an epihalohydrin with an aliphatic diol or a polyalkyleneoxide glycol in the presence of a Lewis acid catalyst followed by conversion of the halohydrin intermediate to the glycidyl ether by reaction with sodium hydroxide. Examples of preferred aliphatic glycidyl ethers include those corresponding to the formulas:



$$\overset{O}{\overbrace{CH_2-CH}}-CH_2-O-(CH_2)_p-O-CH_2-\overset{O}{\overbrace{CH-CH_2}}$$

(IX)



$$\overset{O}{\overbrace{CH_2-CH}}-CH_2-O-(CH_2-\underset{\underset{CH_3}{|}}{CH}-O)_q-CH_2-\overset{O}{\overbrace{CH-CH_2}}$$

(X)

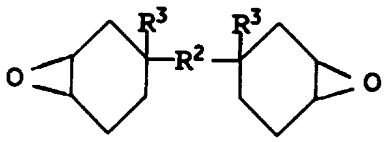
wherein:

p is an integer from 2 to 12, preferably from 2 to 6; and

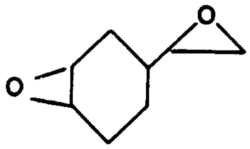
q is an integer from 4 to 24, preferably from 4 to 12.

Examples of suitable aliphatic glycidyl ethers include for example, diglycidyl ethers of 1,4 butanediol, neopentyl glycol, cyclohexane dimethanol, hexanediol, polypropylene glycol, and like diols and glycols; and triglycidyl ethers of trimethylol ethane and trimethylol propane.

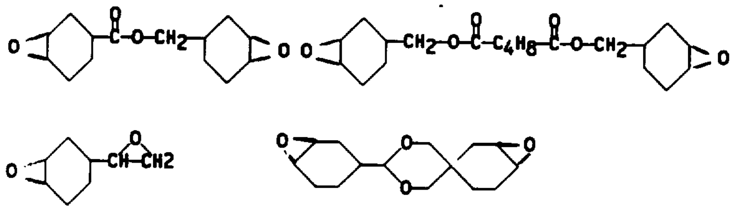
Cycloaliphatic epoxies can be produced by epoxidizing a cycloalkene-containing compound with greater than one olefinic bond with peracetic acid. Examples of the preferred cycloaliphatic epoxies include those corresponding to the formulas:



or

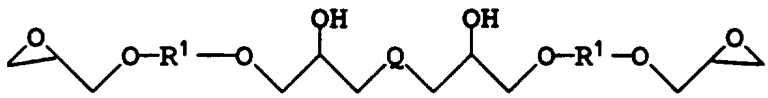


wherein R^2 is a divalent aliphatic group optionally containing ether or ester groups or together with R^3 or R^4 form a spiro ring optionally containing heteroatoms, and R^3 and R^4 are independently hydrogen or R^3 or R^4 together with R^2 form a spiro ring optionally containing heteroatoms such as oxygen. Preferably R^2 contains about 1 to 20 carbon atoms. Examples of cycloaliphatic epoxies include, for example, 3,4-epoxycyclohexylmethyl-(3,4-epoxy)cyclohexane carboxylate, dicycloaliphatic diether diepoxy [2-(3,4-epoxy)cyclohexyl-5,5-spiro-(3,4-epoxy)-cyclohexane-m-dioxane], bis(3,4-epoxycyclohexylmethyl)adipate, bis(3,4-epoxycyclohexyl)adipate and vinylcyclohexene dioxide [4-(1,2-epoxyethyl)-1,2-epoxy-cyclohexane]. Cycloaliphatic epoxies include compounds of the formulas:



Commercial examples of preferred epoxy resins include, for example, EPON Resins DPL-862, 828, 826, 825, 1001, EPONEX Resin 1510, HELOXY Modifiers 107, 67, 68, and 32 (EPON, EPONEX and HELOXY are trademarks) all available from Shell Chemical Company and Union Carbide Epoxy Resins ERL-4221, -4289, -4299, -4234 and -4206.

The carboxylic acid is contacted with the epoxy resin under conditions effective to react the acid group and the epoxide group and to produce epoxy-functional polyethers represented by the formulas:



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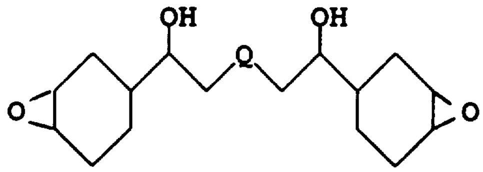

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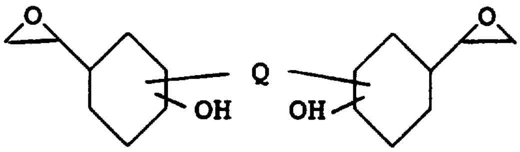

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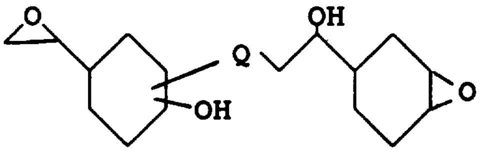

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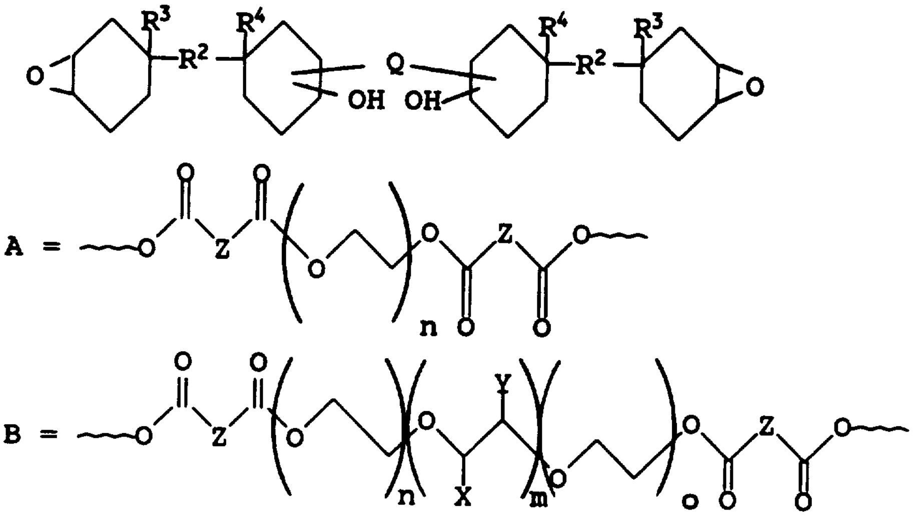


(V)

wherein Q is A or B, R^1 is independently a divalent hydrocarbon group, said divalent hydrocarbon groups having 8 to 120 carbon atoms, X and Y are independently a hydrogen, methyl or ethyl group with the provision that if X is methyl or ethyl, Y is hydrogen or if Y is methyl or ethyl, X is hydrogen and m+n+o is a positive real number from 1 to 450, R^2 is a divalent aliphatic group optionally containing ether or ester groups or together with R^3 or R^4 form a spiro ring optionally containing heteroatoms, and R^3 and R^4 are independently hydrogen or R^3 or R^4 together with R^2 form a spiro ring optionally containing heteroatoms such as oxygen. The location of the OH and Q bonding to the cycloaliphatic ring represents the different isomers formed by the cycloaliphatic ring opening reaction. It can be appreciated that the diacid Q moiety can be attached to either para- or meta- position from R^2 or epoxy moiety.

Typically, the mole ratio of the carboxylic acid to epoxy resin is within the range of from 1:2, more preferably from 1:3 to 1:20, more preferably to 1:10. The reaction is typically carried out at a temperature from ambient temperature to an elevated temperature sufficient to react the acid group and the epoxide group which is typically within the range of from 25 °C, preferably from 60 °C, to 150 °C, preferably to 130 °C for a time effective to produce the reaction products. The progress of the reaction can be monitored and targeted to produce the desired product by measuring the acid equivalent weight and the epoxy equivalent weight of the reactant mixture. Generally, the reaction mixture is heated until an acid equivalent weight of the mixture indicates that greater or equal than 99% of the original number of equivalents of acid is consumed, and at least an equivalent amount of epoxies is consumed which is generally one hour or greater. For cycloaliphatic epoxies, the monitoring of the course of reaction by following consumption of epoxy alone can be misleading, due to competing homopolymerization of this type of epoxy group. Preferably, this reaction is carried out in the presence of a catalyst.

The reaction typically produces a product which contains molecules which result from the condensation of two molecules of diepoxides with one molecule of diacid, as well as other oligomeric species or unreacted epoxide depending on the mole or equivalent ratios of the epoxy resin to the carboxylic acid groups and the amount of time the reaction is allowed to proceed. The reaction may be stopped before completion, in which case monoepoxy monoacid species will be present in the product mixture. Preferably, excess of the epoxy resin (mole ratio of the epoxy resin to carboxylic acid being greater than 2:1) is used to minimize the formation of the polyesterified species. If desired the diepoxide product or a mixture containing predominantly diepoxide product (diepoxide being the largest component in the mixture) can be recovered from the reaction mixture by conventional techniques.

The catalysts are bases or metal chelates such as, for example, ammonium compounds, phosphonium compounds, tertiary amines, and phosphines. Examples of more preferred catalysts include, for example, triphenylphosphonium acid acetate, ethyltriphenyl phosphonium iodide, benzyldimethylamine, triphenylphosphine, tributylamine, aluminum salicylates, tetramethylammonium hydroxide and the like. The amount of catalyst present is preferably from 0.005, more preferably from 0.01, to 1.0, more preferably to 0.5 weight percent based on the total weight of the epoxy resin and the carboxylic acid.

Examples 1-7 demonstrate the preparation of the diacid terminated polyalkylene glycols. Examples 8-16 demonstrate the preparation of the epoxy-functional polyethers of the invention.

Polyethylene glycols (PEG) used in the examples below were obtained from Fluka Chemical Co. EPON Resin 828 (a diglycidyl ether of dihydric phenol having epoxy equivalent weight of 186-188) and EPONEX Resin 1510 (a hydrogenated diglycidyl ether of dihydric phenol having epoxy equivalent weight of 220) were obtained from Shell Chemical Company.

EXAMPLE 1

Preparation of diacid terminated Polyethylene Glycol 6000.

Into a 500-ml flask were added 200.0 g of a polyethylene glycol (PEG) of molecular weight (MW) 6,000 (Fluka) and an equivalent amount (11.2 g) of 4-methylhexahydrophthalic anhydride (MHHPA). Under agitation the mixture was heated to 110 °C and held for 2 hours to prepare a diacid terminated material of equivalent weight 3,168.

EXAMPLE 2

Preparation of diacid terminated Polyethylene Glycol 6000.

Into a 500-ml flask were added 200.0 g of a PEG of MW 6,000 (Fluka) and an equivalent amount (11.2 g) of MHHPA. Under agitation the mixture was heated to 110 °C and held for 2 hours to prepare a diacid terminated material of equivalent weight 3,168.

EXAMPLE 3

Preparation of diacid terminated Polyethylene Glycol 8000.

Into a 500-ml flask were added 150.0 g of a PEG of MW 8,000 (Fluka) and an equivalent amount (6.3 g) of MHHPA. Under agitation the mixture was heated to 110 °C and held for 2 hours to prepare a diacid terminated material of equivalent weight 4,168.

EXAMPLE 4

Preparation of diacid terminated Polyethylene Glycol 3000.

Into a 500-ml flask were added 200.1 g of a PEG of MW 3,000 (Fluka) and an equivalent amount (22.4 g) of MHHPA. Under agitation the mixture was heated to 110 °C and held for 2 hours to prepare a diacid terminated material of equivalent weight 1,668.

EXAMPLE 5

Preparation of diacid terminated Polyethylene Glycol 10000.

Into a 500-ml flask were added 200.0 g of a PEG of MW 10,000 (Fluka) and an equivalent amount (6.7 g) of MHHPA. Under agitation the mixture was heated to 110 °C and held for 2 hours to prepare a diacid terminated material of equivalent weight 5,168.

EXAMPLE 6

Preparation of diacid terminated Block Copolymer of Polyethylene Glycol and Polypropylene Glycol.

Into a 500-ml flask were added 100.1 g of a polyethylene glycol/polypropylene glycol block copolymer of MW 11,400 (PLURONIC F88 available from BASF (PLURONIC is a trademark)) and an equivalent amount (3.0 g) of MHHPA. Under agitation the mixture was heated to 110 °C and held for 1.5 hours to prepare a diacid terminated material of equivalent weight 5,868.

EXAMPLE 7

Preparation of diacid terminated Polyethylene Glycol 3000.

Into a 500-ml flask were added 200.0 g of a PEG of MW 3,000 (Fluka) and an equivalent amount (22.4 g) of MHHPA. Under agitation the mixture was heated to 110 °C and held for 2 hours to prepare a diacid terminated material of equivalent weight 1,668.

EXAMPLE 8

Preparation of Epoxy Resin Modified with Diacid Terminated Polyethylene Glycol 6000 (Residual Unreacted Acid).

Into a 500-ml flask were added 150.1 g of the product from Example 1 and 44.3 g (5 equivalents) of a bisphenol-A epoxy resin (EPON Resin 828 from Shell Chemical Company) having an equivalent weight of 186 g/eq. Under agitation, the mixture was heated to 100 °C, and 0.056 g of ethyltriphenylphosphonium iodide was added. The mixture was held at 100 °C for 1.5 hours to prepare a material with an acid value of 0.102 meq/g. n = 136.

EXAMPLE 9

Preparation of Epoxy Resin Modified with Diacid Terminated Polyethylene Glycol 6000 (Residual Unreacted Acid).

Into a 500-ml flask were added 150.0 g of the product from Example 2, 88.7 g (10 equivalents) of a bisphenol-A epoxy resin (EPON Resin 828 from Shell Chemical Company) having an equivalent weight of 186 g/eq, and 0.061 g of ethyltriphenylphosphonium iodide. Under agitation, the mixture was heated to 100 °C and held for 1.5 hours to prepare the modified resin with an acid value of 0.067 meq/g. n = 136.

EXAMPLE 10

Preparation of Epoxy Resin Modified with Diacid Terminated Polyethylene Glycol 8000 (Residual Unreacted Acid).

Into a 500-ml flask were added 125.0 g of the product from Example 3, 56.1 g (10 equivalents) of a bisphenol-A epoxy resin (EPON Resin 828 from Shell Chemical Company) having an equivalent weight of 186 g/eq, and 0.034 g of ethyltriphenylphosphonium iodide. Under agitation, the mixture was heated to 100 °C and held for 1.5 hours to prepare the modified resin with an acid value of 0.104 meq/g. n = 182.

EXAMPLE 11

Preparation of Epoxy Resin Modified with Diacid Terminated Polyethylene Glycol 3000 (Residual Unreacted Acid).

Into a 500-ml flask were added 150.0 g of the product from Example 4, 168.2 g (19 equivalents) of a bisphenol-A epoxy resin (EPON Resin 828 from Shell Chemical Company) having an equivalent weight of 186 g/eq, and 0.070 g of ethyltriphenylphosphonium iodide. Under agitation, the mixture was heated to 100 °C and held for 1.5 hours to prepare the modified resin with an acid value of 0.122 meq/g. n = 68.

EXAMPLE 12

Preparation of Epoxy Resin Modified with Diacid Terminated Polyethylene Glycol 10000 (Residual Unreacted Acid).

Into a 500-ml flask were added 100.0 g of the product from Example 5, 36.1 g (10 equivalents) of a bisphenol-A epoxy resin (EPON Resin 828 from Shell Chemical Company) having an equivalent weight of 186 g/eq, and 0.033 g of ethyltriphenylphosphonium iodide. Under agitation, the mixture was heated to 100 °C and held for 1.5 hours to prepare the modified resin with an acid value of 0.047 meq/g. n = 227.

EXAMPLE 13

Preparation of Epoxy Resin Modified with Diacid Terminated Block Copolymer of Polyethylene Glycol and Polypropylene Glycol (Complete Reaction of Acid).

Into a 500-ml flask were added 84.0 g of the product from Example 6, 53.6 g (20 equivalents) of a bisphenol A epoxy resin (EPON Resin 828 from Shell Chemical Company) having an equivalent weight of 186 g/eq, and 0.028 g of ethyltriphenylphosphonium iodide. Under agitation, the mixture was heated to 100 °C and held for 2.0 hours to prepare the modified resin with an acid value of <0.001 meq/g. n = 104, m = 39 and o = 104.

EXAMPLE 14

Preparation of Epoxy Resin Modified with Diacid Terminated Polyethylene Glycol 6000 (Complete Reaction of Acid).

The product from Example 9 was placed into an oven heated to 130 °C and held for 0.5 hours to prepare the modified resin with an acid value of <0.001 meq/g. n = 136.

EXAMPLE 15

Preparation of Epoxy Resin Modified with Diacid Terminated Polyethylene Glycol 3000 (Complete Reaction of Acid).

The product from Example 11 was placed into an oven heated to 130 °C and held for 1.0 hours to prepare the modified resin with an acid value of <0.001 meq/g. n = 68.

EXAMPLE 16

Preparation of Epoxy Resin Modified with Diacid Terminated Polyethylene Glycol 3000 (Complete Reaction of Acid).

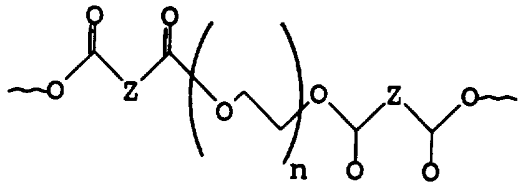
Into a 500-ml flask were added 168.2 g of the product from Example 7, 150.0 g (8 equivalents) of a bisphenol A epoxy resin (EPON Resin 828 from Shell Chemical Company) having an equivalent weight of 186 g/eq, and 0.065 g of ethyltriphenylphosphonium iodide. Under agitation, the mixture was heated to 100 °C and held for 2.0 hours to prepare the modified resin with an acid value of <0.01 meq/g. $n = 68$.

CLAIMS

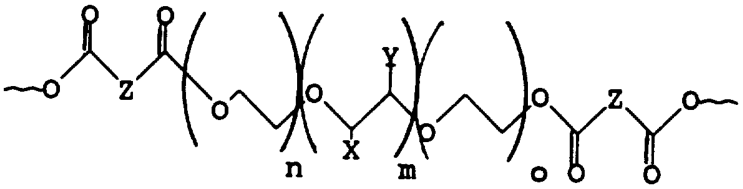
1. A composition comprising a product produced by reacting (a) a carboxylic acid having the formula:

$$H\text{-}Q\text{-}H \qquad (VI)$$

A =



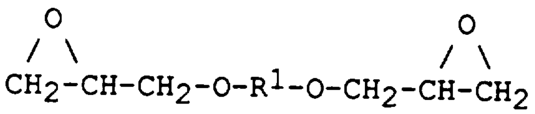
B =



wherein Q is A or B, Z is a C_{1-20} hydrocarbylene moiety, X and Y are independently a hydrogen, methyl or ethyl group with the provision that if X is methyl or ethyl, Y is hydrogen or if Y is methyl or ethyl, X is hydrogen, and n+m+o is a positive real number from 1 to 450 and (b) an epoxy resin having a functionality of at least 1.5 epoxide group per molecule in a carboxylic acid to epoxy resin mole ratio of from 1:2 to 1:20.

2. The composition of claim 1 wherein n+m+o is a positive real number from 6 to 200.

3. The composition of claim 1 wherein the epoxy resin has the formula

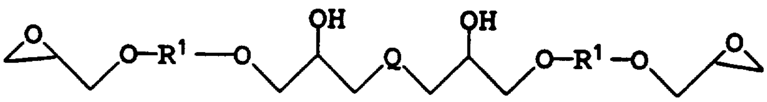


$$\overset{O}{\overbrace{CH_2\text{-}CH}}\text{-}CH_2\text{-}O\text{-}R^1\text{-}O\text{-}CH_2\text{-}\overset{O}{\overbrace{CH\text{-}CH_2}} \qquad (VIII)$$

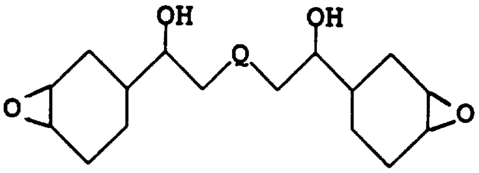
wherein R^1 is divalent aliphatic, divalent cycloaliphatic, divalent aryl, or divalent arylaliphatic group.

4. The composition of claim 1 wherein the epoxy resin is a diglycidyl ether of a dihydric phenol or a diglycidyl ether of a hydrogenated dihydric phenol.

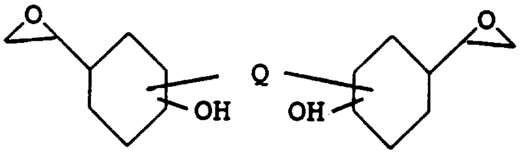
5. Epoxy-functional polyether having the formula:



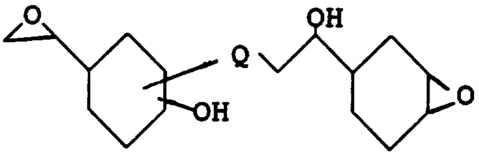
(I)



(II)

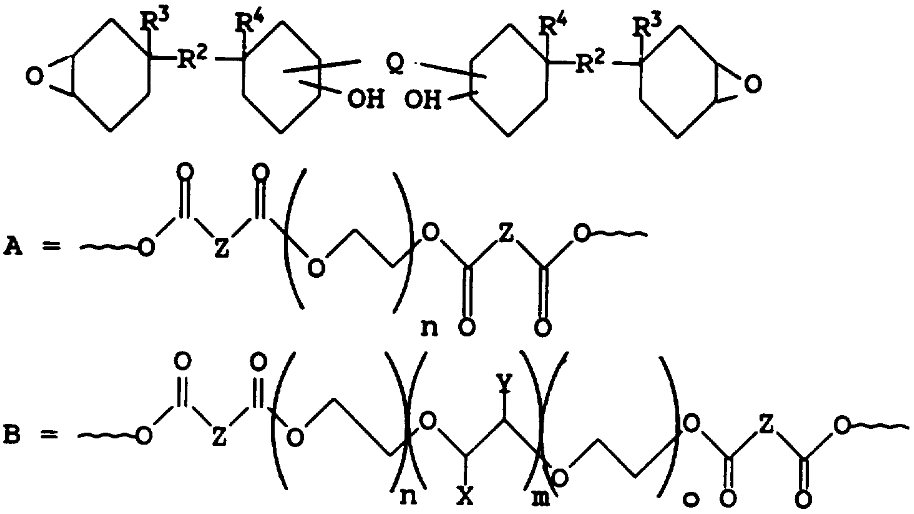


(III)



(IV)

or



(V)

wherein Q is A or B, R^1 is independently a divalent hydrocarbon group, X and Y are independently a hydrogen, methyl or ethyl group with the provision that if X is methyl or ethyl, Y is hydrogen or if Y is methyl or ethyl, X is hydrogen, Z is a C_{1-20} hydrocarbylene moiety, and m+n+o is a positive real number from 1 to 450, R^2 is a divalent aliphatic group optionally containing ether or ester groups or together with R^3 or R^4 form a spiro ring optionally containing heteroatoms, and R^3 and R^4 are independently hydrogen or R^3 or R^4 together with R^2 form a spiro ring optionally containing heteroatoms such as oxygen.

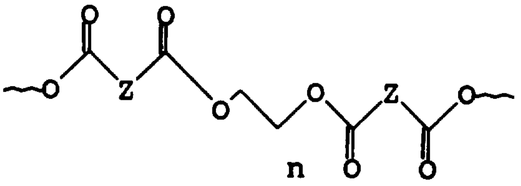
6. The compound of claim 17 wherein n+m+o is an integer from 6 to 200.

7. A composition comprising a compound according to claim 5 or 6.

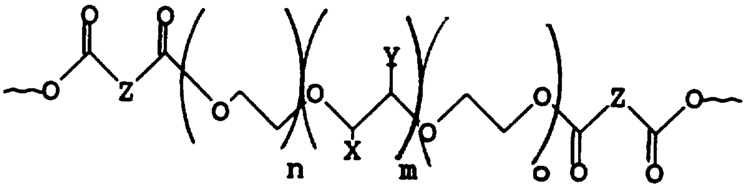
8. A method for producing an epoxy-functional polyether comprising reacting a carboxylic acid having the formula:

$$H\text{-}Q\text{-}H \qquad \text{(VI)}$$

A =



B =



wherein Q is A or B, Z is a hydrocarbylene moiety, X and Y are independently a hydrogen, methyl or ethyl group with the provision that if X is methyl or ethyl, Y is hydrogen or if Y is methyl or ethyl, X is hydrogen, and n+m+o is a positive real number from 1 to 450 and an epoxy resin having a functionality of at least 1.5 epoxide group per molecule in a carboxylic acid to epoxy resin mole ratio of from 1:2 to 1:20 under conditions effective to react the acid group and the epoxide group.

9. The method of claim 10 wherein the carboxylic acid and the epoxy resin are reacted at a temperature within the range of 25 °C to 150 °C in the presence of a base or a metal chelate.

10. The method of claim 9 wherein the carboxylic acid and the epoxy resin are reacted in the presence of a catalyst selected from the group consisting of ammonium compounds, phosphonium compounds, tertiary amines, and phosphines.

INTERNATIONAL SEARCH REPORT

Intr onal Application No
PCT/EP 95/05161

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08G59/12 C08L63/00 C08L71/02 C08G65/32

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 C08L

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	GB,A,2 113 690 (GOLDSCHMIDT TH.) 10 August 1983 see claim 1; table 1 see page 3, line 60 - line 64 ---	1-10
X	CH,A,410 431 (MINNESOTA MINING AND MANUFACTURING CO.) 31 October 1966 see examples 1-7 see claim 1 ---	1-10
X	US,A,4 497 945 (SALLOUM R.J. ET AL) 5 February 1985 see claims 1-5 see column 5, line 60 - line 65 see column 3, line 14 - line 20 --- -/--	1-10

☒ 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

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Date of the actual completion of the international search 18 April 1996	Date of mailing of the international search report 15. 05. 96
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 O'Sullivan, T

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

Inv onal Application No
PCT/EP 95/05161

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP,A,0 581 599 (MORTON INTERNATIONAL INC.) 2 February 1994 see claim 1 see example 5; table 1	1-10
A	CH,A,454 455 (CIBA AG.) 28 June 1968 see claim 1 see column 3, line 34 - line 36	1,5
A	EP,A,0 618 245 (HOECHST AG) 5 October 1994 see claim 1	1-10

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INTERNATIONAL SEARCH REPORT

Information on patent family members

In' ional Application No
PCT/EP 95/05161

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		FR-A- 2520368	29-07-83
CH-A-410431		CH-A- 410430	
		DE-B- 1096600	
		DE-B- 1096602	
		GB-A- 857073	
		US-A- 3523143	04-08-70
US-A-4497945	05-02-85	NONE	
EP-A-0581599	02-02-94	US-A- 5356715	18-10-94
		AU-B- 3993393	10-02-94
		CA-A- 2097795	01-02-94
		JP-A- 6157768	07-06-94
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		FR-A- 1491254	16-11-67
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		CA-A- 2119170	30-09-94
		JP-A- 6340729	13-12-94
		US-A- 5459180	17-10-95