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(54) Titre : COMPOSITIONS D'AGENT D'EXTENSION DE CHAINE DE DIAMINE
(54) Title: DIAMINE CHAIN EXTENDER COMPOSITIONS

(57) Abrégé/Abstract:
This invention provides chain extender compositions. These compositions comprise (i) an aromatic primary diamine, and (ii) a component selected from the group consisting of: (a) an aliphatic secondary diamine; (b) an aliphatic primary diamine; (c) an aliphatic secondary diamine and an aliphatic primary diamine; (d) a diimine; and (e) a combination of any two or more of (a) through (d). When (ii) is (a), (a) has amino hydrocarbyl groups which are secondary or tertiary hydrocarbyl groups; when (ii) is (d), and (d) is an aromatic diimine, each imino hydrocarbylidene group has at least two carbon atoms. Processes for producing polyurethanes, polyureas, and polyurea-urethanes are also provided.

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(54) Title: DIAMINE CHAIN EXTENDER COMPOSITIONS

(57) Abstract: This invention provides chain extender compositions. These compositions comprise (i) an aromatic primary diamine, and (ii) a component selected from the group consisting of: (a) an aliphatic secondary diamine; (b) an aliphatic primary diamine; (c) an aliphatic secondary diamine and an aliphatic primary diamine; (d) a diimine; and (e) a combination of any two or more of (a) through (d). When (ii) is (a), (a) has amino hydrocarbyl groups which are secondary or tertiary hydrocarbyl groups; when (ii) is (d), and (d) is an aromatic diimine, each imino hydrocarbylidene group has at least two carbon atoms. Processes for producing polyurethanes, polyureas, and polyurea-urethanes are also provided.

hydrocarbylidene group has at least two carbon atoms. Preferred components for use with the aromatic primary diamine are aliphatic secondary diamines. The components can be present in the chain extender composition in a variety of proportions; the preferred ratios vary with the type of component from (ii).

I. Component (i)

[0010] Aromatic primary diamines are component (i) of the chain extender compositions of the invention.

[0011] One type of aromatic primary diamine that can be used in this invention is an aromatic primary diamine in which at least one position ortho to each amino group has a hydrogen atom as a substituent, and which aromatic primary diamine is either in the form of one phenyl ring having two amino groups on the ring or in the form of two phenyl rings connected by an alkylene bridge and having one amino group on each ring. The phenyl rings may have, but need not have, one or more hydrocarbyl groups on the phenyl ring(s). Hydrocarbyl groups, when present on the phenyl rings, may be the same or different. When both amino groups are on one phenyl ring, the amino groups may be in any position relative to each other on the ring; preferably, the amino groups are meta or para relative to each other. When the amino groups are on two phenyl rings connected by an alkylene bridge, they may be in any position on the rings; preferably, each amino group is meta or para relative to the alkylene bridge. The alkylene bridge of the two-ring diamine has from one to six carbon atoms; preferably, the alkylene bridge has from one to three carbon atoms. More preferably, the alkylene bridge has one or two carbon atoms; highly preferred is an alkylene bridge having one carbon atom. The hydrocarbyl groups, when present on the phenyl ring(s), are as described above for the aromatic diimines. When one or more hydrocarbyl groups are present on the phenyl ring(s), the hydrocarbyl groups can have from one to twenty carbon atoms; preferably, the hydrocarbyl groups have from one to six carbon atoms.

[0012] Suitable aromatic primary diamines of this type having both amino groups on one phenyl ring include, but are not limited to, 1,2-benzenediamine, 1,3-benzenediamine, 1,4-benzenediamine, 4-ethyl-1,2-benzenediamine, 2-isopropyl-1,3-benzenediamine, 4-tert-butyl-1,3-benzenediamine, 2-pentyl-1,4-benzenediamine, 4,5-dihexyl-1,2-benzenediamine, 4-methyl-5-heptyl-1,3-benzenediamine, 4,6-di-n-propyl-1,3-benzenediamine, 2,5-dioctyl-1,4-benzenediamine, 2,3-diethyl-1,4-benzenediamine, and 4,5,6-tribexyl-1,3-benzenediamine.

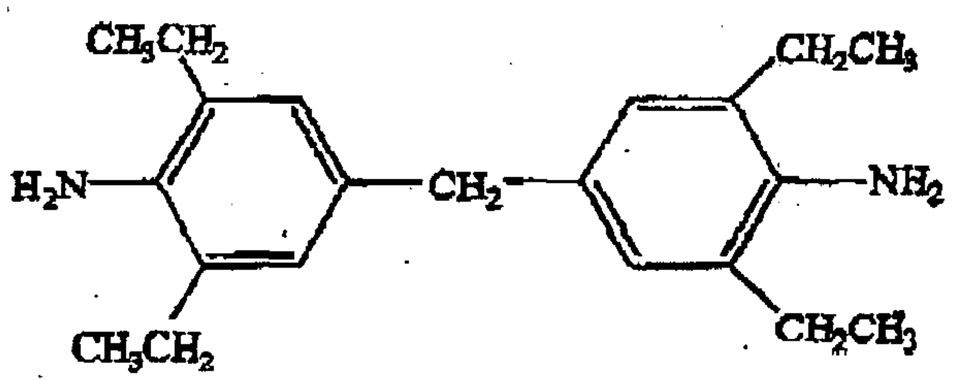
[0013] Examples of suitable aromatic primary diamines of this type in which one amino group is on each of two phenyl rings include 2,2'-methylenebis(benzeneamine), 2,3'-methylenebis-(benzeneamine), 2,4'-methylenebis(benzeneamine), 3,3'-methylenebis(benzeneamine), 3,4'-methylenebis(benzeneamine), 4,4'-methylenebis(benzeneamine), 4,4'-(1,2-ethanediyl)bis-(benzeneamine), 3,4'-(1,3-

propanediyl)bis(benzeneamine), 2,2'-methylenebis(5-tert-butyl-benzeneamine), 3,3'-methylenebis(2-methylbenzeneamine), 3,3'-methylenebis(5-pentylbenzeneamine), 3,3'-methylenebis(6-isopropylbenzeneamine), 4,4'-methylenebis(2-methylbenzeneamine), 4,4'-methylenebis(3-sec-butylbenzeneamine), 4,4'-(1,2-ethanediyl)bis(2-methylbenzeneamine), 3,3'-methylenebis(2,4-dipentylbenzeneamine), 3,3'-methylenebis(5,6-diisopropylbenzeneamine), 4,4'-methylenebis(2,3-di-sec-butylbenzeneamine), 4,4'-methylenebis(3,5-di-tert-butylbenzeneamine), and the like.

[0014] Another type of aromatic primary diamine that can be used in this invention, which is a preferred type of aromatic primary diamine, is an aromatic primary diamine in which each position ortho (immediately adjacent) to an amino group bears a hydrocarbyl group, and which aromatic primary diamine either is in the form of one phenyl ring having two amino groups on the ring, which amino groups are meta or para relative to each other, or is in the form of two phenyl rings connected by an alkylene bridge and having one amino group on each ring. The hydrocarbyl groups on the phenyl rings (adjacent to the amino groups) generally have up to twenty carbon atoms, and the hydrocarbyl groups may be the same or different. The alkylene bridge of the two-ring primary diamine has from one to six carbon atoms; preferably, the bridge has from one to three carbon atoms. More preferably, the alkylene bridge has one or two carbon atoms; especially preferred as the alkylene bridge is a methylene group. Particularly preferred hydrocarbyl groups on the phenyl ring(s) are methyl, ethyl, isopropyl, butyl, and mixtures of two or more of these groups. Here, butyl groups include n-butyl, sec-butyl, and t-butyl groups.

[0015] More preferred aromatic primary diamines with two amino groups on one phenyl ring have the amino groups meta relative to each other. Highly preferred hydrocarbyl groups are methyl, ethyl, isopropyl, butyl, and mixtures thereof, where the preference for butyl groups includes n-butyl, sec-butyl, and t-butyl groups. Particularly preferred are aromatic primary diamines in which the hydrocarbyl group between the two meta amino groups is a methyl group, while the two remaining hydrocarbyl groups are ethyl groups, and those in which the hydrocarbyl group between the two meta amino groups is an ethyl group, while one of the two remaining hydrocarbyl groups is a methyl group and the other is an ethyl group, and mixtures thereof. More preferred aromatic primary diamines are also those in which one amino group is on each of two phenyl rings, where the two phenyl rings are connected via an alkylene bridge, and have both amino groups para relative to the alkylene bridge. An especially preferred aromatic primary diamine of this type is a compound where each hydrocarbyl group ortho to an amino group is an ethyl group and the alkylene bridge is a methylene group.

[0016] A preferred aromatic primary diamine is one in which each position ortho to an amino group bears a hydrocarbyl group, and which aromatic primary diamine is in the form of one phenyl ring having two amino groups on the ring, which amino groups are meta or para



which represents another particularly preferred aromatic primary diamine in this invention, can be called 4,4'-methylenbis(2,6-diethylbenzeneamine), 4,4'-methylenbis(2,6-diethylaniline), or 3,3',5,5'-tetraethyl-4,4'-diaminodiphenylmethane.

II. Component (ii)

[0019] Component (ii) is selected from the group consisting of (a) an aliphatic secondary diamine; (b) an aliphatic primary diamine; (c) an aliphatic secondary diamine and an aliphatic primary diamine; (d) a diimine; and (e) a combination of any two or more of (a) through (d). When (ii) is (a), (a) has amino hydrocarbyl groups which are secondary or tertiary hydrocarbyl groups. When (ii) is (d), and (d) is an aromatic diimine, each imino hydrocarbylidene group has at least two carbon atoms. Thus mixtures of subcomponents (a)-(d) in various combinations are within the scope of this invention.

Subcomponent (a)

[0020] Aliphatic secondary diamines which have amino hydrocarbyl groups which are secondary or tertiary hydrocarbyl groups are subcomponent (a) of component (ii). The amino hydrocarbyl groups of the aliphatic secondary diamine can be cyclic or branched. Preferably, the amino hydrocarbyl groups are branched chain alkyl groups having from three to twelve carbon atoms. Examples of suitable amino hydrocarbyl groups include isopropyl, sec-butyl, t-butyl, 3,3-dimethyl-2-butyl, 3-pentyl, cyclopentyl, 4-hexyl, methylcyclohexyl, cyclooctyl, 5-nonyl, and the like.

[0021] The aliphatic secondary diamines are hydrocarbyl secondary diamines where the hydrocarbyl portion of the diamine is aliphatic, where "hydrocarbyl portion" refers to the moiety to which the amino groups are bound. The hydrocarbyl portion of the aliphatic diamine can be cyclic, branched, or straight chain. Cyclic and straight chain are preferred as the hydrocarbyl portion of the aliphatic secondary diamine. When the hydrocarbyl portion of the diamine is cyclic, the cyclic moiety can be a single ring, fused rings, bicyclic rings, or a tricyclic system (which tricyclic system can contain fused rings and/or bicyclic rings). The amino groups may be attached directly to the ring, or one or both amino groups may be bound

to a group that is a substituent of the ring; it is preferred that at least one of the amino groups is bound to the ring. Preferably, the aliphatic secondary diamine has twelve to forty carbon atoms; more preferably, the aliphatic secondary diamine has fifteen to twenty-five carbon atoms. The relative proportions of aromatic primary diamine to aliphatic secondary diamine in the chain extender composition are preferably 0.5:1 to 1:0.5 on an equivalent basis; more preferably, the relative proportions on an equivalent basis are 0.75:1 to 1:0.75. On a weight basis, the relative proportions of aromatic primary diamine to aliphatic secondary diamine in the chain extender composition are preferably 0.25:1 to 5:1; more preferably, the relative proportions on a weight basis are 0.5:1 to 3:1.

[0022] A preferred chain extender composition, when component (ii) is an aliphatic secondary diamine which has amino hydrocarbyl groups which are secondary or tertiary hydrocarbyl groups, in which the hydrocarbyl portion of the aliphatic secondary diamine is a straight chain, has relative proportions of (i) to (ii) on a weight basis of 0.25:1 to 5:1.

[0023] Aliphatic secondary diamines that can be used in this invention include, but are not limited to, N,N'-diisopropylethylenediamine, N,N'-di-sec-butyl-1,2-diaminopropane, N,N'-di(1-cyclopropylethyl)-1,5-diaminopentane, N,N'-di(3,3-dimethyl-2-butyl)-1,5-diamino-2-methylpentane, N,N'-di-sec-butyl-1,6-diaminohexane, N,N'-di(3-pentyl)-2,5-dimethyl-2,5-hexanediamine, N,N'-di(4-hexyl)-1,2-diaminocyclohexane, N,N'-dicyclohexyl-1,3-diaminocyclohexane, N,N'-di(1-cyclobutylethyl)-1,4-diaminocyclohexane, N,N'-di(2,4-dimethyl-3-pentyl)-1,3-cyclohexanebis(methylamine), N,N'-diisopropyl-1,7-diaminoheptane, N,N'-di-sec-butyl-1,8-diaminooctane, N,N'-di(2-pentyl)-1,10-diaminodecane, N,N'-di(3-hexyl)-1,12-diaminododecane, N,N'-di(3-methyl-2-cyclohexenyl)-1,2-diaminopropane, N,N'-di(2,5-dimethylcyclopentyl)-1,4-diaminobutane, N,N'-di(isophoryl)-1,5-diaminopentane, N,N'-di(menthyl)-2,5-dimethyl-2,5-hexanediamine, N,N'-di(5-nonyl)-isophoronediamine, and N,N'-di-(3,3-dimethyl-2-butyl)-3(4),8(9)-bis-(aminomethyl)-tricyclo[5.2.1.0(2,6)]decane (also called N,N'-di-(3,3-dimethyl-2-butyl)-TCD diamine). Preferred aliphatic secondary diamines include N,N'-di-(3,3-dimethyl-2-butyl)-1,6-diaminohexane, N,N'-di-2-(4-methylpentyl)-isophoronediamine, and N,N'-di-(3,3-dimethyl-2-butyl)-TCD diamine.

Subcomponent (b)

[0024] Aliphatic primary diamines are subcomponent (b) of component (ii), and the aliphatic primary diamines used in this invention are hydrocarbyl primary diamines where the hydrocarbyl portion of the diamine is aliphatic. The hydrocarbyl portion of the aliphatic diamine can be cyclic, branched, or straight chain. Preferably, the aliphatic primary diamine has two to twenty carbon atoms; more preferably, the aliphatic primary diamine

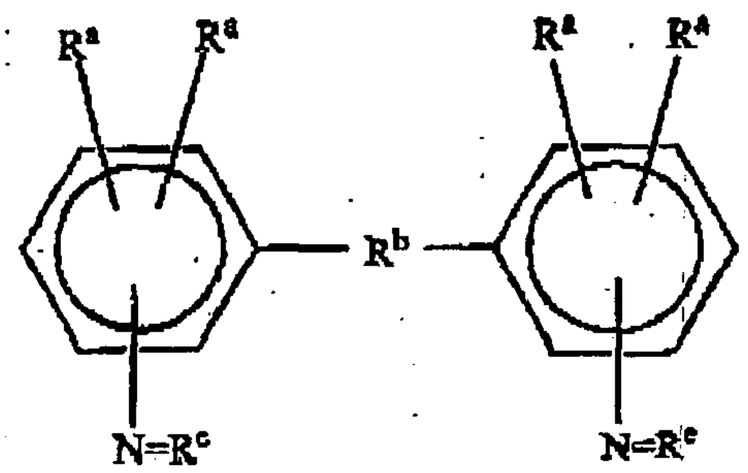
has four to twelve carbon atoms. Particularly preferred aliphatic diamines have cyclic or straight chain hydrocarbyl portions and have four to ten carbon atoms.

[0025] Suitable aliphatic primary diamines include, but are not limited to, ethylenediamine, 1,2-diaminopropane, 1,3-diaminopropane, 1,4-diaminobutane, 1,5-diaminopentane, 1,5-diamino-2-methylpentane, 1,6-diaminohexane, 2,5-dimethyl-2,5-hexanediamine, 1,2-diaminocyclohexane, 1,3-diaminocyclohexane, 1,4-diaminocyclohexane, 2,4-diethyl-6-methyl-1,3-cyclohexanediamine, 4,6-diethyl-2-methyl-1,3-cyclohexanediamine, 1,3-cyclohexanebis(methylamine), 1,4-cyclohexanebis(methylamine), isophorone diamine, bis(p-aminocyclohexyl)methane, bis(3-methyl-4-aminocyclohexyl)methane, 1,8-diamino-p-menthane, 1,7-diaminoheptane, 1,8-diaminooctane, 1,10-diaminodecane, 1,12-diaminododecane, and 3(4),8(9)-bis-(aminomethyl)-tricyclo[5.2.1.0(2,6)]decane (TCD diamine; also called octahydro-4,7-methanoinden-1(2),5(6)-dimethanamine or octahydro-4,7-methano-1H-indenedimethyl-amine). Preferred aliphatic primary diamines include isophorone diamine and TCD diamine.

Subcomponent (c)

[0026] An aliphatic secondary diamine and an aliphatic primary diamine are subcomponent (c) of (ii). The aliphatic secondary diamine and the aliphatic primary diamine can be in any suitable proportion relative to each other, and their combined total amount can be in any relative proportion to the aromatic primary diamine of (i). Preferably, the proportion of the combined total amount of aliphatic secondary diamine and aliphatic primary diamine relative to the aromatic primary diamine of (i) is in the range of 0.5:1 to 1:0.5.

[0027] Suitable aliphatic primary diamines for subcomponent (c) and preferences therefor are as described above for subcomponent (b). Similarly, when the aliphatic secondary diamine of subcomponent (c) has secondary or tertiary amino hydrocarbyl groups, suitable aliphatic secondary diamines and preferences therefor are as described above for subcomponent (a). When the aliphatic secondary diamine of subcomponent (c) is an aliphatic secondary diamine in which the amino hydrocarbyl groups are primary, the hydrocarbyl portion of the aliphatic diamine can be branched, or, preferably, straight chain or cyclic. The amino hydrocarbyl groups of the aliphatic secondary diamine can be cyclic, branched, or straight chain. Preferably, the amino hydrocarbyl groups are straight chain or, more preferably, branched chain alkyl groups having from three to twelve carbon atoms. Examples of suitable amino hydrocarbyl groups include ethyl, propyl, n-butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, dodecyl, and the like. Preferred aliphatic secondary diamines with primary amino hydrocarbyl groups have cyclic or straight chain hydrocarbyl portions and have twelve to twenty-five carbon atoms.



where each R^a may be the same or different, and each R^a is a hydrocarbyl group, R^b is an alkylene bridge, and each R^c is a hydrocarbylidene group having at least two carbon atoms.

[0031] Aromatic diimines that can be used in this invention are aromatic diimines in which the imino hydrocarbylidene groups have at least two carbon atoms. One type of aromatic diimine that can be used in this invention is either in the form of one phenyl ring having two imino groups on the ring, in which each position ortho to an imino group (—N=R) bears a hydrocarbyl group, or in the form of two phenyl rings connected by an alkylene bridge and having one imino group on each ring, in which each position ortho to an imino group bears a hydrocarbyl group. Another type of aromatic diimine that can be used in this invention is an aromatic diimine in which at least one position ortho to each imino group has a hydrogen atom as a substituent, and which aromatic diimine is either in the form of one phenyl ring having two imino groups on the ring or in the form of two phenyl rings connected by an alkylene bridge and having one imino group on each ring.

[0032] The hydrocarbyl groups on the phenyl rings may be the same or different. Examples of suitable hydrocarbyl groups on the aromatic ring include methyl, ethyl, propyl, isopropyl, *n*-butyl, *sec*-butyl, *t*-butyl, pentyl, cyclopentyl, hexyl, methylcyclohexyl, heptyl, octyl, cyclooctyl, nonyl, decyl, dodecyl, phenyl, benzyl, and the like. When the aromatic diimine is in the form of two phenyl rings connected by an alkylene bridge and having one imino group on each ring and the imino group is adjacent (ortho) to the alkylene bridge, the alkylene bridge is considered as a hydrocarbyl group ortho to the imino group. Preferred hydrocarbyl groups on the phenyl ring(s) (ortho to an imino group) of the aromatic diimines are straight-chain or branched-chain alkyl groups having from one to six carbon atoms; particularly preferred hydrocarbyl groups are methyl, ethyl, isopropyl, butyl, and mixtures of two or more of these groups. Here, the preference for butyl groups includes n-butyl, sec-butyl, and t-butyl groups. The alkylene bridge of the two-ringed diimine has from one to six carbon atoms; preferably, the bridge has from one to three carbon atoms. More preferably, the

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alkylene bridge has one or two carbon atoms; highly preferred is an alkylene bridge having one carbon atom, *i.e.*, a methylene group.

[0033] The hydrocarbylidene groups of the imino groups of the aromatic diimine generally have from two to twenty carbon atoms; the hydrocarbylidene groups may be aliphatic (straight chain, branched, or cyclic) or aromatic. Preferably, the imino hydrocarbylidene groups are straight chain or branched chain alkylidene groups having from three to six carbon atoms. Examples of suitable imino hydrocarbylidene groups include ethylidene, propylidene, isopropylidene, 1-cyclopropylethylidene, n-butylidene, sec-butylidene, cyclobutylidene, 2-ethylbutylidene, 3,3-dimethyl-2-butylidene, 3-pentylidene, 3-penten-2-ylidene, cyclopentylidene, 2,5-dimethylcyclopentylidene, 2-cyclopentenylidene, hexylidene, methylcyclohexylidene, menthylidene, ionylidene, phorylidene, isophorylidene, heptylidene, 2,6,-dimethyl-3-heptylidene, cyclooctylidene, 5-nonylidene, decylidene, 10-undecenylidene, benzylidene, 2,4-dimethylbenzylidene, 2-phenylethylidene, 1-phenylpentylidene, 1-naphthylidene, 2-naphthylidene, 1-naphthylethylidene, and the like.

[0034] Preferred aromatic diimines with two imino groups on one phenyl ring have the imino groups meta relative to each other. In these preferred diimines, the imino hydrocarbylidene group preferably is a straight chain or branched chain alkylidene group having from three to six carbon atoms. Particularly preferred are aromatic diimines in which the hydrocarbyl group between the two meta imino groups is a methyl group, while the two remaining hydrocarbyl groups are ethyl groups, and those in which the hydrocarbyl group between the two meta imino groups is an ethyl group, while one of the two remaining hydrocarbyl groups is a methyl group and the other is an ethyl group, and mixtures thereof.

[0035] Preferred aromatic diimines in which one imino group is on each of two phenyl rings, where the two phenyl rings are connected via an alkylene bridge, have both imino groups para relative to the alkylene bridge. A particularly preferred aromatic diimine of this type is a compound where each hydrocarbyl group ortho to an imino group is an ethyl group and the alkylene bridge is a methylene group; this is especially preferred when the imino hydrocarbylidene groups are isopropylidene or sec-butylidene.

[0036] Diimines having both imino groups on one phenyl ring suitable for use in this invention include, but are not limited to, N,N'-diisopropylidene-2,4,6-triethyl-1,3-benzenediamine, N,N'-di-sec-butylidene-2,4,6-triethyl-1,3-benzenediamine, N,N'-di(2-pentylidene)-(2,4,6-triethyl-1,3-benzenediamine), N,N'-diisopropylidene-(2,4-diethyl-6-methyl-1,3-benzenediamine), N,N'-di-sec-butylidene-(2,4-diethyl-6-methyl-1,3-benzenediamine), N,N'-diisopropylidene-(4,6-diethyl-2-methyl-1,3-benzenediamine), N,N'-di-sec-butylidene-(4,6-diethyl-2-methyl-1,3-benzenediamine), N,N'-dicyclobutylidene-(4,6-diethyl-2-methyl-1,3-benzenediamine), N,N'-dicyclopentylidene-(2,4-diisopropyl-6-methyl-1,3-benzenediamine), N,N'-diisopropylidene-(2-methyl-4,6-di-sec-butyl-1,3-benzenediamine),

N,N'-di(undecylidene)-3,4'-(1,3-propanediyl)bis(benzeneamine), N,N'-di(2,4-dimethyl-3-pentylidene)-2,2'-methylenebis(5-tert-butylbenzeneamine), N,N'-di(phorylidene)-3,3'-methylenebis(5-pentylbenzeneamine), N,N'-di(3-methylbutylidene)-3,3'-methylenebis(6-isopropylbenzeneamine), N,N'-di(2-heptylidene)-4,4'-methylenebis(2-methylbenzeneamine), N,N'-dimenthylidene-4,4'-methylenebis(3-sec-butylbenzeneamine), N,N'-di(1-cyclopentylethylidene)-4,4'-(1,2-ethanediyl)bis(2-methylbenzeneamine), and N,N'-di(1-penten-3-ylidene)-4,4'-methylenebis(2,3-di-sec-butylbenzeneamine).

[0039] Aliphatic diimines are also part of subcomponent (d) of the curative mixture. The hydrocarbyl portion of the aliphatic diimine can be cyclic, branched, or straight chain hydrocarbyl group, where "hydrocarbyl portion" refers to the moiety to which the imino groups are bound. Preferably, the aliphatic diimine has six to forty carbon atoms; more preferably, the aliphatic diimine has ten to thirty carbon atoms. The hydrocarbylidene groups of the imino groups of the aliphatic diimine generally have from one to twenty carbon atoms; the hydrocarbylidene groups may be straight chain, branched, or cyclic. Preferably, the imino hydrocarbylidene groups are straight chain or branched chain alkylidene groups having from three to six carbon atoms. Examples of suitable imino hydrocarbylidene groups include ethylidene, propylidene, isopropylidene, 1-cyclopropylethylidene, n-butylidene, sec-butylidene, cyclobutylidene, 2-ethylbutylidene, 3,3-dimethyl-2-butylidene, 3-pentylidene, 3-penten-2-ylidene, cyclopentylidene, 2,5-dimethylcyclopentylidene, 2-cyclopentenylidene, hexylidene, methylcyclohexylidene, menthylidene, ionylidene, phorylidene, isophorylidene, heptylidene, 2,6,-dimethyl-3-heptylidene, cyclooctylidene, 5-nonylidene, decylidene, 10-undecenylidene, and the like.

[0040] Aliphatic diimines that can be used in this invention include, but are not limited to, N,N'-diisopropylidene-ethylenediamine, N,N'-di-sec-butylidene-1,2-diaminopropane, N,N'-di(2-butenylidene)-1,3-diaminopropane, N,N'-di(1-cyclopropylethylidene)-1,5-diaminopentane, N,N'-di(3,3-dimethyl-2-butylidene)-1,5-diamino-2-methylpentane, N,N'-di-sec-butylidene-1,6-diaminohexane, N,N'-di(3-pentylidene)-2,5-dimethyl-2,5-hexanediamine, N,N'-di(4-hexylidene)-1,2-diaminocyclohexane, N,N'-dicyclohexylidene-1,3-diaminocyclohexane, N,N'-di(1-cyclobutylethylidene)-1,4-diaminocyclohexane, N,N'-di(2,4-dimethyl-3-pentylidene)-1,3-cyclohexanebis(methylamine), N,N'-di(1-penten-3-ylidene)-1,4-cyclohexanebis(methylamine), N,N'-diisopropylidene-1,7-diaminoheptane, N,N'-di-sec-butylidene-1,8-diaminooctane, N,N'-di(2-pentylidene)-1,10-diaminodecane, N,N'-di(3-hexylidene)-1,12-diaminododecane, N,N'-di(3-methyl-2-cyclohexenylidene)-1,2-diaminopropane, N,N'-di(2,5-dimethylcyclopentylidene)-1,4-diaminobutane, N,N'-di(isophorylidene)-1,5-diaminopentane, N,N'-di(menthylidene)-2,5-dimethyl-2,5-hexanediamine, N,N'-di(undecylidene)-1,2-diaminocyclohexane, N,N'-di-2-(4-methylpentylidene)-isophoronediamine, and N,N'-di(5-nonylidene)-isophoronediamine.

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Processes of the Invention

[0041] In the processes of the invention, a polymer which is a polyurethane, polyurea, or polyurea-urethane is made by mixing together at least one aromatic isocyanate, at least one polyol and/or at least one polyetheramine, and a chain extender composition of the invention. As is well known in the art, other components may also be included when making the polyurethane, polyurea, or polyurethane-urea, such as one or more flame retardants, thermal stabilizers, and/or surfactants. In some processes of the invention, the polyol or polyetheramine, chain extender composition, and when used, optional ingredients, are blended together to form a first mixture, followed by blending this first mixture with the isocyanate to form a second mixture; this second mixture is allowed to cure. In other processes of this invention, the isocyanate and the polyol or polyetheramine are blended together to form a prepolymer, which prepolymer is then mixed together with the chain extender composition to form the desired polymer. In still other processes of the invention, the isocyanate is mixed with polyol or polyetheramine to form a quasiprepolymer; polyol or polyetheramine is mixed with the chain extender composition to form a mixture; and then the mixture is mixed with the quasiprepolymer to form the desired polymer. Thus, the chain extender composition is reacted with an aromatic polyisocyanate and at least one polyol and/or at least one polyetheramine or with a prepolymer or a quasiprepolymer of the isocyanate and the polyol or polyetheramine. In the practice of this invention, use of quasiprepolymers is preferred way of producing polyureas.

[0042] The aromatic polyisocyanates are organic polyisocyanates having at least two isocyanate groups. Generally, the isocyanates have a free –NCO content of at least 0.1% by weight. Aromatic polyisocyanates that can be used in the practice of this invention include phenylene diisocyanate, toluene diisocyanate (TDI), xylene diisocyanate, 1,5-naphthalene diisocyanate, chlorophenylene 2,4-diisocyanate, bitoluene diisocyanate, dianisidine diisocyanate, tolidine diisocyanate, alkylated benzene diisocyanates, methylene-interrupted aromatic diisocyanates such as methylenediphenyl diisocyanates, especially 4,4-methylenediphenyl diisocyanate (MDI), alkylated analogs of methylene-interrupted aromatic diisocyanates (such as 3,3'-dimethyl-4,4'-diphenylmethane diisocyanate), and polymeric methylenediphenyl diisocyanates. A preferred aromatic polyisocyanate is 4,4-methylenediphenyl diisocyanate (MDI). Examples of isocyanates that can be used are also taught in, for example, U.S. 4,595,742.

[0043] Isocyanate-reactive polyols and polyetheramines (sometimes referred to as amine-terminated polyols) that are typically used in making polyurethanes, polyureas, and polyurea-urethanes range in molecular weight from 60 to over 6,000. The polyols can be dihydric, trihydridic, or polyhydric polyols, but are usually dihydric. Examples of suitable polyols include poly(ethyleneoxy) glycols, dipropylene glycol, poly(propyleneoxy) glycols,

dibutylene glycol, poly(butyleneoxy) glycols, and the polymeric glycol from caprolactone, commonly known as polycaprolactone. The polyetheramines used to make polyurethanes, polyureas, and polyurea-urethanes are amine-capped polyols which are the reaction product of a polyol and then an amine with alkylene oxides as well as amine-capped hydroxyl-containing polyesters. Polyetheramines typically have a molecular weight of 200 to 6000. Several commercially available polyetheramines known as Jeffamines® available from Huntsman Chemical Company and include Jeffamine® T-5000, a polypropylene oxide triamine of 5000 molecular weight, XTJ-509, a polypropylene oxide triamine of 3000 molecular weight, XTJ-510, a polypropylene oxide diamine of 4000 molecular weight, and Jeffamine® D-2000, a polypropylene oxide diamine of 2000 molecular weight. Jeffamine® T-5000 and Jeffamine® D-2000 are preferred polyetheramines in the practice of this invention.

[0044] In a preferred process of the invention, the polyisocyanate is 4,4-methylenediphenyl diisocyanate. In another preferred process of the invention, at least one polyetheramine is used. In still another preferred process of the invention, component (i) of the chain extender composition is aromatic primary diamine in which each position ortho to an amino group bears a hydrocarbyl group, and which aromatic primary diamine is in the form of one phenyl ring having two amino groups on the ring, which amino groups are meta or para relative to each other, and in which the aromatic primary diamine has amino groups are meta relative to each other, and/or the ortho hydrocarbyl groups are methyl, ethyl, isopropyl, butyl, or mixtures thereof.

Polymers formed by the Invention

[0045] The polymers formed by the invention are polyurethanes, polyureas, and polyurea-urethanes (sometimes called polyurea-polyurethanes). Because of their differing gel times (cure rates), these polmers can be used in different applications. Polyurethanes, polyureas, and polyurea-urethanes made with the chain extender compositions of the invention have more desirable gel times, and, at a minimum, the physical properties of the polymers are not adversely affected by theuse of the chain extender compositions of the invention. In fact, an improvement in the tensile strength of the polymers made from chain extender compositions of the invention is observed in comparison to polymers made with the individual chain extenders.

[0046] A preferred polymer formed by this invention is formed from 4,4-methylenediphenyl diisocyanate; another preferred polymer formed by this invention is formed from at least one polyetheramine. Another preferred polymer formed by this invention is formed from a chain extender composition of the invention in which component (i) is an aromatic primary diamine in which each position ortho to an amino group bears a hydrocarbyl group, and which

[0054] It is to be understood that the reactants and components referred to by chemical name or formula anywhere in this document, whether referred to in the singular or plural, are identified as they exist prior to coming into contact with another substance referred to by chemical name or chemical type (e.g., another reactant, a solvent, or *etc.*). It matters not what preliminary chemical changes, transformations and/or reactions, if any, take place in the resulting mixture or solution or reaction medium as such changes, transformations and/or reactions are the natural result of bringing the specified reactants and/or components together under the conditions called for pursuant to this disclosure. Thus the reactants and components are identified as ingredients to be brought together in connection with performing a desired chemical operation or reaction or in forming a mixture to be used in conducting a desired operation or reaction. Also, even though an embodiment may refer to substances, components and/or ingredients in the present tense ("is comprised of", "comprises", "is", *etc.*), the reference is to the substance, component or ingredient as it existed at the time just before it was first contacted, blended or mixed with one or more other substances, components and/or ingredients in accordance with the present disclosure.

[0055] Also, even though the may refer to substances in the present tense (e.g., "comprises", "is", *etc.*), the reference is to the substance as it exists at the time just before it is first contacted, blended or mixed with one or more other substances in accordance with the present disclosure.

[0056] Except as may be expressly otherwise indicated, the article "a" or "an" if and as used herein is not intended to limit, and should not be construed as limiting, the description or a to a single element to which the article refers. Rather, the article "a" or "an" if and as used herein is intended to cover one or more such elements, unless the text expressly indicates otherwise.

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CLAIMS

1. A chain extender composition which comprises

(i) an aromatic primary diamine, and

(ii) a component selected from the group consisting of

(a) an aliphatic secondary diamine;

(c) an aliphatic secondary diamine and an aliphatic primary diamine;

(d) a diimine; and

(e) a combination of any two or more of (a) through (d),

with the proviso that when (ii) is (a), (a) has amino hydrocarbyl groups which are secondary or tertiary hydrocarbyl groups, and with the proviso that when (ii) is (d), and (d) is an aromatic diimine, each imino hydrocarbylidene group has at least two carbon atoms.

2. A composition as in Claim 1 wherein (i) is an aromatic primary diamine in which each position ortho to an amino group bears a hydrocarbyl group, and which aromatic primary diamine either is in the form of one phenyl ring having two amino groups on the ring, which amino groups are meta or para relative to each other, or is in the form of two phenyl rings connected by an alkylene bridge and having one amino group on each ring.

4. A composition as in Claim 1 wherein (i) is a mixture of 2,4-diethyl-6-methyl-1,3-benzenediamine and 4,6-diethyl-2-methyl-1,3-benzenediamine.

5. A composition as in Claim 1 wherein (ii) is an aliphatic secondary diamine which has amino hydrocarbyl groups which are secondary or tertiary hydrocarbyl groups, wherein the hydrocarbyl portion of the aliphatic secondary diamine either has a single ring, in which at least one of the amino groups is bound directly to a ring, or wherein the hydrocarbyl portion of the aliphatic secondary diamine is a straight chain.

7. A composition as in Claim 1 wherein (ii) is N,N'-di-(3,3-dimethyl-2-butyl)-1,6-diaminohexane, N,N'-di-2-(4-methylpentyl)-isophoronediamine, or N,N'-di-(3,3-dimethyl-2-butyl)-TCD diamine.

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9. A composition as in Claim 1 wherein (ii) is an aliphatic secondary diamine and an aliphatic primary diamine, and wherein said aliphatic primary diamine has at least one of the following features:

the hydrocarbyl portion of the diamine is cyclic or a straight chain;

the aliphatic primary diamine has about four to about ten carbon atoms.

10. A composition as in Claim 1 wherein (ii) is an aliphatic secondary diamine and an aliphatic primary diamine, and wherein the aliphatic secondary diamine either

has amino hydrocarbyl groups which are secondary or tertiary hydrocarbyl groups, wherein the hydrocarbyl portion of the aliphatic secondary diamine has a single ring, wherein at least one of the amino groups is bound directly to a ring; or

has amino hydrocarbyl groups which are secondary or tertiary hydrocarbyl groups, wherein the hydrocarbyl portion of the aliphatic secondary diamine is a straight chain.

11. A composition as in Claim 1 wherein (ii) is an aliphatic secondary diamine and an aliphatic primary diamine, and wherein said aliphatic secondary diamine is N,N'-di-(3,3-dimethyl-2-butyl)-1,6-diaminohexane, N,N'-di-2-(4-methylpentyl)-isophoronediamine, or N,N'-di-(3,3-dimethyl-2-butyl)-3(4),8(9)-bis-(aminomethyl)-tricyclo[5.2.1.0(2,6)]decane.

12. A composition as in Claim 1 wherein (ii) is an aromatic diimine which is either in the form of one phenyl ring having two imino groups on the ring, in which each position ortho to an imino group bears a hydrocarbyl group, or is in the form of two phenyl rings connected by an alkylene bridge and having one imino group on each ring, in which each position ortho to an imino group bears a hydrocarbyl group.

13. A process for producing a polymer, which process comprises mixing together (A) at least one aromatic polyisocyanate, (B) at least one polyol and/or at least one polyetheramine, and (C) a chain extender comprised of

(i) an aromatic primary diamine, and

(ii) a component selected from the group consisting of:

(a) an aliphatic secondary diamine;

(c) an aliphatic secondary diamine and an aliphatic primary diamine;

(d) a diimine; and

(e) a combination of any two or more of (a) through (d),

with the proviso that when (ii) is (a), (a) has amino hydrocarbyl groups which are secondary or tertiary hydrocarbyl groups, and with the proviso that when (ii) is (d), and (d) is an aromatic diimine, each imino hydrocarbylidene group has at least two carbon atoms.

14. A process as in Claim 13 wherein said polyisocyanate is 4,4-methylenediphenyl diisocyanate, and wherein (B) is at least one polyetheramine.

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15. A process as in Claim 13 wherein (i) is an aromatic primary diamine in which each position ortho to an amino group bears a hydrocarbyl group, and which aromatic primary diamine either is in the form of one phenyl ring having two amino groups on the ring, which amino groups are meta or para relative to each other, or is in the form of two phenyl rings connected by an alkylene bridge and having one amino group on each ring.

17. A process as in Claim 13 wherein (i) is a mixture of 2,4-diethyl-6-methyl-1,3-benzenediamine and 4,6-diethyl-2-methyl-1,3-benzenediamine.

18. A process as in Claim 13 wherein (ii) is an aliphatic secondary diamine which has amino hydrocarbyl groups which are secondary or tertiary hydrocarbyl groups, wherein the hydrocarbyl portion of the aliphatic secondary diamine either has a single ring, and wherein at least one of the amino groups is bound directly to a ring, or wherein the hydrocarbyl portion of the aliphatic secondary diamine is a straight chain.

20. A process as in Claim 13 wherein (ii) is N,N'-di-(3,3-dimethyl-2-butyl)-1,6-diaminohexane, N,N'-di-2-(4-methylpentyl)-isophoronediamine, or N,N'-di-(3,3-dimethyl-2-butyl)-TCD diamine.

22. A process as in Claim 13 wherein (ii) is an aliphatic secondary diamine and an aliphatic primary diamine, and wherein the aliphatic secondary diamine either

has amino hydrocarbyl groups which are secondary or tertiary hydrocarbyl groups, wherein the hydrocarbyl portion of the aliphatic secondary diamine has a single ring, wherein at least one of the amino groups is bound directly to a ring; or

has amino hydrocarbyl groups which are secondary or tertiary hydrocarbyl groups, wherein the hydrocarbyl portion of the aliphatic secondary diamine is a straight chain.

23. A process as in Claim 13 wherein (ii) is an aliphatic secondary diamine and an aliphatic primary diamine, and wherein said aliphatic secondary diamine is N,N'-di-(3,3-dimethyl-2-butyl)-1,6-diaminohexane, N,N'-di-2-(4-methylpentyl)-isophoronediamine, or N,N'-di-(3,3-dimethyl-2-butyl)-3(4),8(9)-bis-(aminomethyl)-tricyclo[5.2.1.0(2,6)]decane.

24. A process as in Claim 13 wherein a quasiprepolymer is formed during the process

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, or wherein a prepolymer is formed during the process.

26. A polymer which is formed from ingredients comprising (A) at least one aromatic polyisocyanate, (B) at least one polyol and/or at least one polyetheramine, and (C) a chain extender comprised of

(i) an aromatic primary diamine, and

(ii) a further component selected from the group consisting of:

(a) an aliphatic secondary diamine;

(c) an aliphatic secondary diamine and an aliphatic primary diamine;

(d) a diimine; and

(e) a combination of any two or more of (a) through (d),

with the proviso that when (ii) is (a), (a) has amino hydrocarbyl groups which are secondary or tertiary hydrocarbyl groups, and with the proviso that when (ii) is (d), and (d) is an aromatic diimine, each imino hydrocarbylidene group has at least two carbon atoms.

27. A polymer as in Claim 26 wherein said polyisocyanate is 4,4-methylenediphenyl diisocyanate, and wherein (B) is at least one polyetheramine.

28. A polymer as in Claim 26 wherein (i) is an aromatic primary diamine in which each position ortho to an amino group bears a hydrocarbyl group, and which aromatic primary diamine either is in the form of one phenyl ring having two amino groups on the ring, which amino groups are meta or para relative to each other, or is in the form of two phenyl rings connected by an alkylene bridge and having one amino group on each ring.

30. A polymer as in Claim 26 wherein (i) is a mixture of 2,4-diethyl-6-methyl-1,3-benzenediamine and 4,6-diethyl-2-methyl-1,3-benzenediamine.

31. A polymer as in Claim 26 wherein (ii) is an aliphatic secondary diamine which has amino hydrocarbyl groups which are secondary or tertiary hydrocarbyl groups, wherein the hydrocarbyl portion of the aliphatic secondary diamine has a single ring, in which at least one of the amino groups is bound directly to a ring, or wherein the hydrocarbyl portion of the aliphatic secondary diamine is a straight chain.

33. A polymer as in Claim 26 wherein (ii) is N,N'-di-(3,3-dimethyl-2-butyl)-1,6-diaminohexane, N,N'-di-2-(4-methylpentyl)-isophoronediamine, or N,N'-di-(3,3-dimethyl-2-butyl)-TCD diamine.

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35. A polymer as in Claim 26 wherein (ii) is an aliphatic secondary diamine and an aliphatic primary diamine, and wherein the aliphatic secondary diamine either

has amino hydrocarbyl groups which are secondary or tertiary hydrocarbyl groups, wherein the hydrocarbyl portion of the aliphatic secondary diamine has a single ring, and at least one of the amino groups is bound directly to a ring; or

has amino hydrocarbyl groups which are secondary or tertiary hydrocarbyl groups, and the hydrocarbyl portion of the aliphatic secondary diamine is a straight chain.

36. A polymer as in Claim 26 wherein (ii) is an aliphatic secondary diamine and an aliphatic primary diamine, and wherein said aliphatic secondary diamine is N,N'-di-(3,3-dimethyl-2-butyl)-1,6-diaminohexane, N,N'-di-2-(4-methylpentyl)-isophoronediamine, or N,N'-di-(3,3-dimethyl-2-butyl)-3(4),8(9)-bis-(aminomethyl)-tricyclo[5.2.1.0(2,6)]decane.

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