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(54) Title: CHAIN EXTENDERS

(57) **Abstract:** This invention provides chain extender compositions. These compositions comprise aliphatic secondary diamines in which the amino hydrocarbyl groups are different from each other. Processes for producing polyurethanes, polyureas, and polyurea-urethanes using these aliphatic secondary diamines are also provided.

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CHAIN EXTENDERS

TECHNICAL FIELD

5 [0001] This invention relates to the use of aliphatic diamines to form polyurethanes, polyureas, and polyurea-urethanes.

BACKGROUND

10 [0002] There are many polyfunctional compounds, including diols and aromatic diamines, which are indicated to be useful as chain extenders in the preparation of polyurethane, polyurea, and polyurethane-urea polymers and/or as curing agents for epoxy resins. None of these compounds has a reactivity such as to make it universally ideal, and many fail to provide satisfactory properties in the products made by their use. Thus, there is still a need to find compounds capable of serving as chain extenders or curing agents. U.S. Pat. No. 4,806,616 teaches the use of certain N,N'-dialkylphenylenediamines as chain extenders in
15 preparing polyurethanes and polyureas. In this connection, also see for example U.S. 4,528,363, which teaches the use of secondary aliphatic diamines as part of a resin binder, and U.S. 6,218,480 B1, which discloses use of aromatic diamines as hardeners for polyurethanes. Secondary aromatic diamines have also been used as anti-degradants for rubber; see U.S. 4,900,868.

20 [0003] There is a growing need for chain extenders with slower cure rates, so it would be a further advantage if aliphatic diamines exhibited slower curing rates than those of presently available chain extenders.

SUMMARY OF THE INVENTION

25 [0004] This invention in part provides chain extenders which are aliphatic secondary diamines. These diamines, when included in formulations for polyurethanes, polyureas, and polyurea-urethanes, produce such polymers at desired cure rates and having desirable physical properties.

30 [0005] One embodiment of this invention provides a composition which comprises an aliphatic secondary diamine in which the amino hydrocarbyl groups are different from each other.

[0006] Another embodiment of this invention is a process for preparing aliphatic secondary diamines in which the amino hydrocarbyl groups are different from each other. The process

comprises mixing together a) a hydrogenation agent, b) at least one aliphatic primary diamine, and c) at least two different ketones, or at least two different aldehydes, or at least one ketone and at least one aldehyde, such that an aliphatic secondary diamine in which the amino hydrocarbyl groups are different from each other is formed.

- 5 [0007] Still another embodiment of this invention is a process for producing a polymer which is a polyurethane, polyurea, or polyurea-urethane. The process comprises mixing together at least (A) an aliphatic polyisocyanate, (B) at least one polyol and/or at least one polyetheramine, and (C) an aliphatic secondary diamine in which the amino hydrocarbyl groups are different from each other.
- 10 [0008] Yet another embodiment of this invention is a polymer which is a polyurethane, polyurea, or polyurea-urethane, which polymer is formed from ingredients comprising at least (A) an aliphatic polyisocyanate, (B) at least one polyol and/or at least one polyetheramine, and (C) an aliphatic secondary diamine in which the amino hydrocarbyl groups are different from each other.
- 15 [0009] These and other embodiments and features of this invention will be still further apparent from the ensuing description and appended claims.

FURTHER DETAILED DESCRIPTION OF THE INVENTION

20 Compositions of the Invention

[0010] Compositions of this invention are made up of aliphatic secondary diamines in which the two amino hydrocarbyl groups are different from each other. What is meant by the phrase "the two amino hydrocarbyl groups are different from each other" is that the hydrocarbyl group on one nitrogen atom in the aliphatic secondary diamine molecule is
25 different from the hydrocarbyl group on the other nitrogen atom in the same aliphatic secondary diamine molecule. It is to be understood that the compositions of the invention, because of the way they are prepared, often also contain minor amounts of aliphatic secondary diamines in which the amino hydrocarbyl groups are the same.

[0011] The aliphatic secondary diamines which are compositions of this invention are
30 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 secondary diamine can be cyclic, branched, or, preferably, straight chain. The amino hydrocarbyl groups of the aliphatic secondary diamine

can be cyclic, branched, or straight chain. Preferably, the amino hydrocarbyl groups are cyclic and/or branched chain alkyl groups having from three to about twelve carbon atoms. Examples of suitable amino hydrocarbyl groups include ethyl, propyl, isopropyl, n-butyl, sec-butyl, t-butyl, 3,3-dimethyl-2-butyl, pentyl, 3-methyl-2-pentyl, 4-methyl-2-pentyl, cyclopentyl, hexyl, cyclohexyl, methylcyclohexyl, heptyl, octyl, cyclooctyl, nonyl, decyl, dodecyl, and the like. Preferred amino hydrocarbyl groups include isopropyl, cyclohexyl, and 3,3-dimethyl-2-butyl. Preferably, the aliphatic secondary diamine has about eight to about forty carbon atoms; more preferably, the aliphatic secondary diamine has about ten to about thirty carbon atoms. Particularly preferred aliphatic secondary diamines have cyclic or straight chain hydrocarbyl portions, have cyclic or branched chain amino hydrocarbyl groups, and have about twelve to about twenty-five carbon atoms.

[0012] Aliphatic secondary diamines of the invention include, but are not limited to, N-ethyl,N'-isopropyl-ethylenediamine, N-isopropyl,N'-sec-butyl-1,2-diaminopropane, N-isopropyl,N'-(2-butenyl)-1,3-diaminopropane, N-cyclopentyl,N'-isopropyl-1,4-diaminobutane, N-sec-butyl,N'-3-hexyl-1,4-diaminobutane, N-sec-butyl,N'-5-nonyl-1,5-diaminopentane, N-isopropyl,N'-cyclohexyl-1,5-diaminopentane, N-cyclopentyl,N'-(3,3-dimethyl-2-butyl)-1,5-diamino-2-methylpentane, N-isopropyl,N'-(3,3-dimethyl-2-butyl)-1,6-diaminohexane, N-isopropyl,N'-cyclohexyl-1,6-diaminohexane, N-cyclohexyl,N'-(3,3-dimethyl-2-butyl)-1,6-diaminohexane, N-cyclohexyl,N'-(4-methyl-2-pentyl)-1,6-diaminohexane, N-sec-butyl,N'-methylcyclohexyl-1,6-diaminohexane, N-isopropyl,N'-cyclopentyl-1,6-diaminohexane, N-(3-pentyl),N'-cyclohexyl-2,5-dimethyl-2,5-hexanediamine, N-isopropyl,N'-(3-hexyl)-1,2-diaminocyclohexane, N-sec-butyl,N'-cyclohexyl-1,3-diaminocyclohexane, N-(3,3-dimethyl-2-butyl),N'-cyclopentyl-1,4-diaminocyclohexane, N-sec-butyl,N'-cyclopentyl-1,3-cyclohexanebis(methylamine), N-isopropyl,N'-cyclohexyl-1,4-cyclohexanebis(methylamine), N-isopropyl,N'-(3,3-dimethyl-2-butyl)-1,7-diaminoheptane, N-sec-butyl,N'-cyclohexyl-1,8-diaminooctane, N-isopropyl,N'-(2-pentyl)-1,10-diaminodecane, N-sec-butyl,N'-(3-hexyl)-1,12-diaminododecane, N-isopropyl,N'-cyclopentyl-isophoronediamine, and N-(5-nonyl),N'-cyclohexyl-isophoronediamine. Preferred aliphatic secondary diamines include N-isopropyl,N'-(3,3-dimethyl-2-butyl)-1,6-diaminohexane, N-isopropyl,N'-cyclohexyl-1,6-diaminohexane, N-cyclohexyl,N'-(4-methyl-2-pentyl)-1,6-diaminohexane, and N-cyclohexyl,N'-(3,3-dimethyl-2-butyl)-1,6-diaminohexane.

Synthesis Processes of the Invention

[0013] In the processes of the invention in which an aliphatic secondary diamine in which the amino hydrocarbyl groups are different from each other is formed (the "synthesis processes"), a) a hydrogenation agent, b) at least one primary aliphatic diamine, and c) at least two different ketones, or at least two different aldehydes, or at least one ketone and at least one aldehyde are mixed together to form the aliphatic secondary diamine in which the amino hydrocarbyl groups are different from each other.

I. Components used in the Processes of the Invention

A. Ketones and aldehydes

[0014] To form an aliphatic secondary diamine in which the amino hydrocarbyl groups are different from each other, at least two different ketones, or at least two different aldehydes, or at least one ketone and at least one aldehyde are used. While the use of two ketones, two aldehydes, or one ketone and one aldehyde is preferred, mixtures may be employed. Such mixtures can include, for example, three or more ketones, three or more aldehydes, two ketones and one aldehyde, or one ketone and two aldehydes.

[0015] The ketones and aldehydes used in the processes of this invention are hydrocarbyl ketones and hydrocarbyl aldehydes. The hydrocarbyl portion of the ketone or aldehyde is aliphatic (cyclic, branched, or straight chain), preferably cyclic or a branched chain. Preferably, the ketones and aldehydes used in the practice of this invention have from three to about twenty carbon atoms. More preferred are ketones and aldehydes having from three to about fifteen carbon atoms. Especially preferred ketones and aldehydes have a hydrocarbyl portion which is cyclic or a branched aliphatic group, and have from three to about ten carbon atoms.

[0016] The overall mole ratio of the ketone(s) and/or aldehyde(s) to the aliphatic primary diamine is normally at least about one mole of ketone and/or aldehyde per mole of amino group, *i.e.*, at least about two moles of ketone and/or aldehyde per mole of diamine. Since there is at least one ketone and/or aldehyde for each of the two amino groups, there is usually and preferably at least about one mole of ketone and/or aldehyde per mole of amino group. Thus, when there are only two ketones and/or aldehydes, or only one ketone and one aldehyde, there is usually and preferably at least about one mole of each ketone or aldehyde per mole of amino group. In some instances, an excess of ketone(s) and/or aldehyde(s) is used, typically about a 5% to about a 10% molar excess of ketone or aldehyde relative to the

primary diamine.

[0017] Suitable ketones include acetone (2-propanone), methyl ethyl ketone (2-butanone), 2-pentanone, 3-pentanone, 2-hexanone, 3-hexanone, 2-heptanone, 4-heptanone, 3-octanone, 4-octanone, 3-nonanone, 5-nonanone, 2-undecanone, 6-undecanone, di-n-hexyl ketone, 8-pentadecanone, 9-heptadecanone, 10-nonadecanone, cyclobutanone, cyclopentanone, cyclohexanone, cyclopropyl methyl ketone (1-(cyclopropyl)ethanone), cyclobutyl methyl ketone, cyclopentyl methyl ketone, cyclohexyl methyl ketone, 3-methyl-2-pentanone, 4-methyl-2-pentanone (methyl isobutyl ketone), cyclopentanone, 2-methyl-cyclopentanone, 3-methyl-cyclopentanone, 5-methyl-2-hexanone, 4-methyl-3-heptanone, 3,3-dimethyl-2-butanone (methyl tert-butyl ketone), 2,4-dimethyl-3-pentanone, cyclohexanone, 2,6-dimethyl-3-heptanone, 3,5-dimethyl-4-heptanone, 2-methylcyclohexanone, 2,5-dimethylcyclopentanone, menthone, isophorone, and the like. Preferred ketones include acetone, methyl ethyl ketone, 3,3-dimethyl-2-butanone, 4-methyl-2-pentanone, cyclohexanone, 4-heptanone, and 5-nonanone. Acetone, cyclohexanone, 4-methyl-2-pentanone, and 3,3-dimethyl-2-butanone are particularly preferred ketones in the practice of this invention.

[0018] Aldehydes that can be used in the practice of this invention include acetaldehyde, propionaldehyde, butyraldehyde, valeraldehyde (pentanal), isovaleraldehyde, hexanal, cyclohexanecarboxaldehyde, heptaldehyde, octyl aldehyde, nonyl aldehyde, decyl aldehyde, undecyl aldehyde, dodecyl aldehyde, 2-ethylbutyraldehyde, undecylenic aldehyde (10-undecenal), and the like.

[0019] Usually, the ketone and/or aldehyde is in liquid form when it is used in the processes of the invention. For some ketones and aldehydes, elevated temperatures and/or increased pressure will liquefy the ketone or aldehyde. If such conditions are not used, a solvent may be used to provide the ketone or aldehyde in liquid form.

B. Hydrogenation agents

[0020] Various hydrogenation agents can be used in the synthesis processes of the invention. Suitable hydrogenation agents that can be used include hydride transfer agents such as sodium cyanoborohydride, sodium borohydride, sodium aluminum hydride, lithium aluminum hydride, and the like; "dissolving metal" reagents such as Al with alcohol, Al/Hg, Al/Pd with HCl, Na with alcohol, Na/Hg, Mg with alcohol, Fe with HCl, Zn with HCl, Zn/Cu with HCl, Zn/Hg with HCl, Zn/Pd with HCl, Zn/Cu/Pd with HCl, and the like; borane

reductants including BH_3 -pyridine and BH_3 -dimethylamine; and hydrogen with a hydrogenation catalyst, where the hydrogenation catalyst can be platinum on carbon, palladium on carbon, sulfided platinum on carbon, sulfided palladium on carbon, or a mixture of any two or more of these. A preferred type of hydrogenation agent is hydrogen with a hydrogenation catalyst.

[0021] When choosing a hydrogenation agent, especially the "dissolving metal" reagents which are used in conjunction with acid, and hydrogen with a hydrogenation catalyst where acid will be present, it should be remembered that strong acids can cause dimerization and/or polymerization of some ketones.

[0022] When the hydrogenation agent is hydrogen and a hydrogenation catalyst, suitable amounts of hydrogenation catalyst can be relatively low, *i.e.*, in the range of about 0.5 wt% to about 10 wt% relative to the primary diamine. More suitably, in the range of about 0.75 wt% to about 6 wt% hydrogenation catalyst can be used relative to the primary diamine. It has now been found that with the use of greater amounts of the hydrogenation catalyst, the reaction occurs more quickly. Thus, a weight ratio of primary diamine to catalyst in the range of about 20:1 to about 1:20 is feasible, and a weight ratio of primary diamine to hydrogenation catalyst in the range of about 10:1 to about 1:10 is preferred. More preferred is a weight ratio of primary diamine to hydrogenation catalyst in the range of about 1:1 to about 1:5. The use of an amount of catalyst in the preferred ranges provides secondary diamines in high yields in relatively short reaction times.

[0023] The hydrogenation catalyst can be in either powdered form or in granular form. The granular form of the hydrogenation catalyst settles out of solution more readily than does the powdered form, and the granular form tends to have slower reaction rates than are seen with powdered form. However, side reactions are minimized when the hydrogenation catalyst is in granular form. Thus, the preferable form for the hydrogenation catalyst may vary with the particular primary diamine and ketone(s) and/or aldehyde(s) chosen, as minimizing side reactions can be of greater significance in some systems, while in others the increased reaction rate can be more important.

C. Aliphatic primary diamines

[0024] The aliphatic primary diamines used in the processes of 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 about two to about twenty carbon atoms; more preferably, the aliphatic primary diamine has about four to about ten carbon atoms. Particularly preferred aliphatic diamines have cyclic or straight chain hydrocarbonyl portions and have about four to about ten carbon atoms. 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 1,6-diaminohexane. Particularly preferred combinations in the processes of this invention are the use of 1,6-diaminohexane with acetone and cyclohexanone, the use of 1,6-diaminohexane with acetone and 3,3-dimethyl-2-butanone, the use of 1,6-diaminohexane with cyclohexanone and 4-methyl-2-pentanone, and the use of 1,6-diaminohexane with cyclohexanone and 3,3-dimethyl-2-butanone.

D. Solvents

[0025] The ketone(s) and/or aldehyde(s) can serve as the solvent in the processes of the invention; however, one or more solvents can be present during the processes of the invention. The presence of a solvent is not required, but inclusion of a solvent is recommended and preferred. An important consideration in selecting a solvent is that it not interfere with the functioning of the chosen hydrogenation agent; for example, the solvent chosen should not poison the hydrogenation catalyst. Solvent types that can be used include, but are not limited to, liquid aromatic hydrocarbons, liquid aliphatic hydrocarbons, liquid halogenated aliphatic hydrocarbons, ethers, esters, alcohols, and a mixture of two or more solvents.

[0026] Suitable liquid hydrocarbons include benzene, toluene, xylenes, mesitylene, cumene, cymene, pentane, hexane, isohexane, cyclohexane, methylcyclohexane, heptane, octane, cyclooctane, nonane, and the like. Examples of liquid halogenated aliphatic hydrocarbons

that can be used include dichloromethane, trichloromethane, 1,2-dichloroethane, 1-bromo-2-chloroethane, (chloromethyl)cyclopropane, 1-bromobutane, cyclobutyl chloride, neopentyl chloride, 1-bromo-5-chloropentane, cyclopentyl bromide, 1,6-dibromohexane, *trans*-1,2-dichlorocyclohexane, 1-chloroheptane, 1,8-dichlorooctane, and the like. Ethers that are suitable for use in this invention include diethyl ether, di-*n*-propyl ether, diisopropyl ether, di-*n*-butyl ether, butyl ethyl ether, cyclohexylmethyl ether, tetrahydrofuran, 1,3-dioxane, 1,3-dioxolane, glyme (the dimethyl ether of ethylene glycol), 2-methoxyethyl ether (diglyme), and the like. Examples of esters that can be used include ethyl acetate, isopropyl acetate, *n*-butyl acetate, isobutyl acetate, *tert*-butyl acetate, *n*-amyl acetate, isoamyl acetate, hexyl acetate, methyl propionate, ethyl propionate, ethyl butyrate, and the like. Alcohols that can be used in the practice of the invention include methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-methyl-1-propanol, 1-methyl-1-propanol, cyclopropylmethanol, cyclobutanol, cyclopentanol, *cis*-2-methylcyclohexanol, and the like. Preferred solvents when a hydrogenation agent is present include dichloromethane, ethyl acetate, and toluene.

E. Water removal agents

[0027] Without wishing to be bound by theory, in the processes of the invention, it is believed that a diimine is formed as an intermediate, producing water as a by-product, which water is thought to shift the equilibrium toward the ketone(s) and/or aldehyde(s) and the primary diamine; therefore, large amounts of water are normally not desired in such processes. Although it has been found that the presence of water produced in the reaction may be less detrimental than previously believed in the processes of the invention, in at least some instances it may be desirable to minimize the amount of water in the reaction mixture.

[0028] One method for minimizing the amount of water in the reaction mixture is to use a water removal agent. A water removal agent may be included in the reaction mixture to remove water as the water is produced in the process. The only requirement is that the water removal agent not adversely affect the reaction or its products. Suitable water removal agents include molecular sieves, silica gel, calcium chloride, and the like. Molecular sieves are a preferred water removal agent in the practice of this invention.

[0029] An alternative to the use of a water removal agent is the inclusion of a solvent or enough excess ketone or aldehyde to act as the solvent to effectively dilute the water is recommended and preferred. When a solvent is used, a solvent that is able to azeotrope with water and thereby remove water as it is produced during a process is a preferred way of

operating. Particularly preferred solvents that remove water are hexanes and toluene. Another preferred way of operating when using a solvent is to use a solvent which takes water into a phase separate from that in which the reaction is occurring; preferred solvents for this way of operating include toluene and dichloromethane. Both inclusion of a solvent or enough excess ketone or aldehyde to act as the solvent and the use of a water removal agent may be employed to minimize the amount of water. An especially preferred way of operating is to employ enough excess ketone or aldehyde to dilute the water.

II. Conduction of the Synthesis Processes

[0030] Typically, water is not present as an ingredient in the processes of the invention at the start of the process, except for adventitiously present water (*e.g.*, less than about 1 wt% water relative to the total weight of the reaction mass). In this connection, it should be noted that anhydrous conditions are not necessary to the successful conduct of the processes of this invention.

[0031] When the hydrogenation agent is hydrogen and a hydrogenation catalyst, operation under a blanket of hydrogen is preferred. The presence of oxygen is generally not beneficial during the hydrogenation because it is believed that oxygen at least contributes to poisoning of the hydrogenation catalyst. When not operating under a hydrogen atmosphere, the presence of an inert atmosphere comprised of one or more inert gases, such as, for example, nitrogen, helium, or argon is often preferred.

[0032] In the processes of this invention, aliphatic secondary diamines in which the amino hydrocarbyl groups are different from each other are prepared by mixing together a) a hydrogenation agent, b) at least one aliphatic primary diamine, and c) at least two different ketones, or at least two different aldehydes, or at least one ketone and at least one aldehyde.

The process is generally conducted at a temperature in the range of about 20°C to about 140°C and at a pressure in the range of about 1 to about 150 pounds per square inch (9.65×10^4 to 1.03×10^6 Pa). Preferably, temperatures are in the range of about 20°C to about 80°C and pressures are preferably in the range of about 50 to about 125 pounds per square inch (3.45×10^5 to 8.62×10^5 Pa).

[0033] A particularly preferred method for preparing a secondary diamine, when the hydrogenation agent is hydrogen and a hydrogenation catalyst, is to place the primary diamine, hydrogenation catalyst, and solvent in a reaction vessel, and then to seal the reaction vessel under hydrogen gas pressure. The vessel is then heated as desired while the reaction

mixture is stirred. On the laboratory scale, reaction times are typically about five hours to about twenty hours.

III. Workup and recovery from the processes of the invention

5 [0034] The aliphatic secondary diamines produced by the processes of this invention are usually liquids, and can be isolated if desired, or used in non-isolated form. Methods for separating liquids that are well known in the art can be employed to separate at least a portion of the aliphatic secondary diamine from the other components of the reaction mixture. Such methods include, for example, chromatography and distillation; distillation is a preferred
10 separation method. When the aliphatic secondary diamine produced is a solid, standard solid-liquid separation methods such as centrifugation, filtration, or recrystallization can be used to separate at least a portion of the product from the liquid portion of the reaction mixture.

[0035] It is generally economical to recover and recycle excess ketone or aldehyde.
15 Separation of the ketone or aldehyde from the reaction mixture can be performed by distillation, with separation of aqueous portions of any azeotropes encountered, or with decantation of the aqueous layer followed by distillation of the ketone or aldehyde layer. Once at least a portion of the product diimine or secondary diamine has been removed from the reaction mixture, unreacted starting materials can be recycled to the reactor to form a
20 portion of the feed stock.

Polymerization Processes of the Invention

[0036] In the polymerization processes of the invention, a polymer which is a polyurethane, polyurea, or polyurea-urethane is made by mixing together at least one aliphatic
25 polyisocyanate, at least one polyol and/or at least one polyetheramine, and an aliphatic secondary diamine 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, aliphatic secondary diamine
30 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 aliphatic secondary diamine 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 aliphatic secondary diamine composition to form a mixture; and then the mixture is mixed with the quasiprepolymer to form the desired polymer. Thus, the aliphatic secondary diamine composition is reacted with an aliphatic 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.

[0037] The aliphatic polyisocyanates are organic polyisocyanates having at least two isocyanate groups. Generally, the isocyanates have a free -NCO content of at least about 0.1% by weight. Aliphatic polyisocyanates that can be used in the practice of this invention include isophorone diisocyanate (IPDI), cyclohexylene diisocyanate, 4,4'-methylenedicyclohexyl diisocyanate (H12MDI); mixed aralkyl diisocyanates including tetramethylxylyl diisocyanates; and polymethylene isocyanates including 1,4-tetramethylene diisocyanate, 1,5-pentamethylene diisocyanate, 1,6-hexamethylene diisocyanate (HMDI), 1,7-heptamethylene diisocyanate, 2,2,4-and 2,4,4-trimethylhexamethylene diisocyanate, 1,10-decamethylene diisocyanate, and 2-methyl-1,5-pentamethylene diisocyanate. Mixtures of two or more aliphatic polyisocyanates can be used in the practice of this invention. A preferred aliphatic polyisocyanate is isophorone diisocyanate (IPDI). Examples of isocyanates that can be used are also taught in, for example, U.S. 4,595,742.

[0038] 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 about 60 to over 6,000. The polyols can be dihydric, trihydric, 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. Mixtures of two or more polyols can be used in the practice of this invention. 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. Mixtures of two or more polyetheramines can be used in the practice of this invention. Polyetheramines typically have a molecular weight of about 200 to about 6000. Several

commercially available polyetheramines known as Jeffamines[®] available from Huntsman Chemical Company and include Jeffamine[®] T-5000, a polypropylene oxide triamine of about 5000 molecular weight, XTJ-509, a polypropylene oxide triamine of about 3000 molecular weight, XTJ-510, a polypropylene oxide diamine of about 4000 molecular weight, and
5 Jeffamine[®] D-2000, a polypropylene oxide diamine of about 2000 molecular weight. Jeffamine[®] T-5000 and Jeffamine[®] D-2000 are preferred polyetheramines in the practice of this invention.

[0039] In a preferred polymerization process of the invention, the aliphatic secondary diamine composition is N-isopropyl,N'-(3,3-dimethyl-2-butyl)-1,6-diaminohexane. In
10 another preferred polymerization process of the invention, the aliphatic secondary diamine composition is N-isopropyl,N'-cyclohexyl-1,6-diaminohexane. In still another preferred polymerization process of the invention, the aliphatic secondary diamine composition is N-cyclohexyl,N'-(3,3-dimethyl-2-butyl)-1,6-diaminohexane.

15 **Polymers formed by the Invention**

[0040] 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 polymers can be used in different applications. Polyurethanes, polyureas, and polyurea-urethanes made with the aliphatic secondary diamine compositions of the
20 invention have desirable gel times, and, at a minimum, the physical properties of the polymers are not adversely affected by the use of the aliphatic secondary diamine compositions of the invention.

[0041] A preferred polymer formed by this invention is formed from ingredients comprising isophorone diisocyanate, at least one polyetheramine, and an aliphatic secondary diamine in
25 which the hydrocarbyl portion of the aliphatic secondary diamine is a straight chain; and/or the amino hydrocarbyl groups are cyclic and/or branched chain alkyl groups; and/or the aliphatic secondary diamine has about ten to about thirty carbon atoms.

[0042] Another preferred polymer formed by this invention is formed from ingredients comprising an aliphatic secondary diamine which is N-isopropyl,N'-(3,3-dimethyl-2-butyl)-
30 1,6-diaminohexane, or is formed from ingredients comprising an aliphatic secondary diamine which is N-isopropyl,N'-cyclohexyl-1,6-diaminohexane, or is formed from ingredients

comprising an aliphatic secondary diamine which is N-cyclohexyl,N'-(3,3-dimethyl-2-butyl)-1,6-diaminohexane.

[0043] The following example is presented for purposes of illustration, and is not intended to impose limitations on the scope of this invention.

5

EXAMPLE 1

Synthesis of N-cyclohexyl,N'-(4-methyl-2-pentyl)-1,6-diaminohexane

[0044] Ethanol (15 g), 1,6-diaminohexane (12.2 g, 0.105 mol, in 17.4 g aqueous solution), and cyclohexanone (11 g, 0.11 mol) were charged to a flask, and this mixture was stirred at 10 22°C for 10 minutes. Methyl isobutyl ketone (20 g, 0.2 mol) was added to the flask, and the resultant mixture was stirred at 20-65°C for 40 minutes. Wet Pt(S)/C (Engelhard, 3 wt% Pt, 0.61g, 5 wt% to 1,6-diaminohexane) was added to the mixture, which was then purged three times with 95 psig of H₂ at 22°C. The reaction mixture was then heated at 100°C for 4 hrs, then at 120°C for 2 hrs, and then at 125°C for 3 hours, all under 95 psig of H₂. The reaction 15 mixture was cooled and degassed. GC (100°C/5 min./10°C per min. rate/280°C) showed 100% conversion of 1,6-diaminohexane, 58.1% of N-cyclohexyl,N'-2-(4-methyl-pentyl)-1,6-diaminohexane, 22.1% of N,N'-di-cyclohexyl-1,6-diaminohexane, and 19.1% of N,N'-di-2-(4-methyl-pentyl)-1,6-diaminohexane. GC-MS confirmed the identity of N-cyclohexyl,N'-2-(4-methyl-pentyl)-1,6-diaminohexane. Solvent and water were removed from the reaction 20 mixture at 22 to 85°C under vacuum (1-3 mm Hg).

EXAMPLE 2

[0045] In this Example, the isocyanate was isophorone diisocyanate (IPDI; 16.4% NCO). Jeffamine[®] D-2000 (a polyetheramine, Huntsman Chemical) was used to make a polyurea. 25 A two-barrel syringe was used in conjunction with a static mixer. The static mixer had 20 elements and an inner diameter of 0.37 inches (EA 370-20, Ellsworth Adhesives).

[0046] Polyurea formulations containing isocyanate, Jeffamine[®] D-2000, and an aliphatic secondary diamine composition of the invention are prepared. The isocyanate is mixed together with a portion of the Jeffamine[®] D-2000 to form a quasiprepolymer. The remainder 30 of the Jeffamine[®] D-2000 is blended with the aliphatic secondary diamine to form a mixture.

This mixture was then added to one barrel of the two-barrel syringe; the quasiprepolymer was added to the other barrel. The mixture and quasiprepolymer were mixed (reacted) by pushing them through a static mixer onto a steel plate and were cured at room temperature.

[0047] The aliphatic secondary diamine used in the polyurea formulations was N-cyclohexyl,N'-(4-methyl-2-pentyl)-1,6-diaminohexane. Results are summarized in Table 1.

TABLE 1

	Sample 1
B side ingredients	Weight % of B side
N-cyclohexyl,N'-2-(4-methyl-pentyl)-1,6-diaminohexane	54.8
Jeffamine D-2000	29.6
Jeffamine T-5000	8.6
TiO ₂	7.0
A side ingredient	
IPDI (16.4% NCO)	
Properties	
Gel time	8 sec.

[0048] 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.

[0049] 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
5 contacted, blended or mixed with one or more other substances in accordance with the present disclosure.

[0050] 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
10 herein is intended to cover one or more such elements, unless the text expressly indicates otherwise.

[0051] This invention is susceptible to considerable variation in its practice.

CLAIMS

1. An aliphatic secondary diamine composition which comprises an aliphatic secondary diamine in which the amino hydrocarbyl groups are different from each other.

2. A composition as in Claim 1 wherein said composition has at least one of the following features:

the hydrocarbyl portion of the diamine is a straight chain;

the amino hydrocarbyl groups are straight chain or branched chain alkyl groups;

the aliphatic secondary diamine has about ten to about thirty carbon atoms.

3. A composition as in Claim 1 wherein said amino hydrocarbyl groups are selected from the group consisting of isopropyl, 3,3-dimethyl-2-butyl, and cyclohexyl.

4. A composition as in Claim 1 wherein said aliphatic secondary diamine is N-isopropyl,N'-(3,3-dimethyl-2-butyl)-1,6-diaminohexane, N-isopropyl,N'-cyclohexyl-1,6-diaminohexane, N-cyclohexyl,N'-(4-methyl-2-pentyl)-1,6-diaminohexane, or N-cyclohexyl,N'-(3,3-dimethyl-2-butyl)-1,6-diaminohexane.

5. A process for forming an aliphatic secondary diamine in which the amino hydrocarbyl groups are different from each other, which process comprises mixing together

a) a hydrogenation agent,

b) at least one aliphatic primary diamine, and

c) at least two different ketones, or at least two different aldehydes, or at least one ketone and at least one aldehyde,

such that an aliphatic secondary diamine in which the amino hydrocarbyl groups are different from each other is formed.

6. A process as in Claim 5, which process has at least one of the following features:

said hydrogenation agent is hydrogen and a hydrogenation catalyst;

said aliphatic primary diamine is 1,6-diaminohexane;

c) is at least two different ketones, and wherein said ketones are selected from the group consisting of acetone, cyclohexanone, 3,3-dimethyl-2-butanone, and 4-methyl-2-pentanone.

7. A polymer formed from ingredients comprising at least (A) an aliphatic polyisocyanate, (B) at least one polyol and/or at least one polyetheramine, and (C) an aliphatic secondary diamine in which the amino hydrocarbyl groups are different from each other.

8. A polymer as in Claim 7 wherein:
said polyisocyanate is isophorone diisocyanate, and/or
(B) is at least one polyetheramine.

9. A polymer as in Claim 7 wherein said aliphatic secondary diamine has at least
5 one of the following features:

the hydrocarbyl portion of the diamine is a straight chain;
the amino hydrocarbyl groups are straight chain or branched chain alkyl groups;
the aliphatic secondary diamine has about 10 to about thirty carbon atoms.

10. A polymer as in Claim 7 wherein said amino hydrocarbyl groups are selected
10 from the group consisting of isopropyl, 3,3-dimethyl-2-butyl, and cyclohexyl.

11. A polymer as in Claim 7 wherein said aliphatic secondary diamine is N-
isopropyl,N'-(3,3-dimethyl-2-butyl)-1,6-diaminohexane, N-isopropyl,N'-cyclohexyl-1,6-
diaminohexane, N-cyclohexyl,N'-(4-methyl-2-pentyl)-1,6-diaminohexane, or N-
cyclohexyl,N'-(3,3-dimethyl-2-butyl)-1,6-diaminohexane.

12. A process for producing a polymer, which process comprises mixing together
15 at least (A) an aliphatic polyisocyanate, (B) at least one polyol and/or at least one
polyetheramine, and (C) an aliphatic secondary diamine in which the amino hydrocarbyl
groups are different from each other.

13. A process as in Claim 12 wherein:
20 said polyisocyanate is isophorone diisocyanate, and/or
(B) is at least one polyetheramine.

14. A process as in Claim 12 wherein said aliphatic secondary diamine has at least
one of the following features:

the hydrocarbyl portion of the diamine is a straight chain;
25 the amino hydrocarbyl groups are straight chain or branched chain alkyl groups;
the aliphatic secondary diamine has about 10 to about thirty carbon atoms.

15. A process as in Claim 12 wherein said amino hydrocarbyl groups are selected
from the group consisting of isopropyl, 3,3-dimethyl-2-butyl, and cyclohexyl.

16. A process as in Claim 12 wherein said aliphatic secondary diamine is N-
30 isopropyl,N'-(3,3-dimethyl-2-butyl)-1,6-diaminohexane, N-isopropyl,N'-cyclohexyl-1,6-
diaminohexane, N-cyclohexyl,N'-(4-methyl-2-pentyl)-1,6-diaminohexane, or N-
cyclohexyl,N'-(3,3-dimethyl-2-butyl)-1,6-diaminohexane.

17. A process as in Claim 12 or 16 wherein a quasiprepolymer is formed during the process.
18. A process as in Claim 12 wherein a prepolymer is formed during the process.

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2008/053286

A. CLASSIFICATION OF SUBJECT MATTER

INV. C07C209/26 C08G18/32 C08G18/66

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)

C07C C08G

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

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

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 900 868 A (MERZTEN ET AL) 13 February 1990 (1990-02-13) column 1, line 52 - column 4, line 13; claims 1-10; example I	1-18
A	EP 0 420 426 A (TEXACO CHEMICAL) 3 April 1991 (1991-04-03) page 3, line 2 - line 7 page 5, line 20 - line 25; claims 1,8	1-18
A	EP 0 688 802 A (HUNTSMAN) 27 December 1995 (1995-12-27) page 3, line 20 - line 45; claims 1-3,8-11	1-18
A	EP 0 309 980 A (B.F. GOODRICH) 5 April 1989 (1989-04-05) page 4, line 34 - page 6, line 4; claims 1-7; examples 1-3	1

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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