



(51) International Patent Classification:

C08G 18/48 (2006.01) *C08G 18/76* (2006.01)
C08G 18/50 (2006.01) *C08G 18/32* (2006.01)
C08G 18/63 (2006.01) *C08G 73/02* (2006.01)
C08G 18/66 (2006.01)

(21) International Application Number:

PCT/US2016/035642

(22) International Filing Date:

3 June 2016 (03.06.2016)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/182,039 19 June 2015 (19.06.2015) US

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Published:

— with international search report (Art. 21(3))

(54) Title: AUTOCATALYTIC POLYOL USEFUL FOR POLYURETHANE FOAM MANUFACTURE

(57) Abstract: The present invention discloses a tertiary amine initiator and polymeric polyol compositions made therefrom useful for making polyurethane polymers, especially polyurethane foams. Said polyurethane polymer foams demonstrate a good balance of mechanical properties, physical properties, and low emissions. The tertiary amine initiator is one or more partially alkylated amine compound have the Structure II: $RR^1N - (R'-NH)_y - (R'-NR^4)_{x-y} - R' - NR^2R^3$ wherein R' is a C_1 to C_6 linear or branched alkyl group, R , R^1 , R^2 , and R^3 are independently a hydrogen or a C_1 to C_6 linear or branched alkyl group with the proviso that at least one of R , R^1 , R^2 , and R^3 is not hydrogen, R^4 is a hydrogen or a C_1 to C_6 linear or branched alkyl group, x is from 1 to 33, y is from 0 to 32, and z is from 0 to 15, with the proviso that $x-y$ is equal to or greater than 1 and the number of N-H bonds in (II) is greater than 0 and less than 8.



AUTOCATALYTIC POLYOL USEFUL FOR POLYURETHANE FOAM MANUFACTURE

FIELD OF THE INVENTION

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The present invention pertains to novel tertiary amine compositions, initiators made therefrom, and polymeric polyol compositions made therefrom useful for making polyurethane polymers, especially polyurethane foams; said polyurethane polymer foams demonstrating a good balance of mechanical properties, physical properties, and low volatile organic compounds emissions.

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BACKGROUND OF THE INVENTION

Polyether polyols based on the polymerization of alkylene oxides, and/or polyester polyols, are the major components of a polyurethane system together with isocyanates. Polyols can also be filled polyols, such as SAN (styrene/acrylonitrile), PIPA (polyisocyanate polyaddition) or PHD (polyurea) polyols. These systems generally contain additional components such as blowing agents, cross-linkers, chain extenders, surfactants, cell regulators, stabilizers, antioxidants, flame retardant additives, eventually fillers, and typically catalysts such as tertiary amines and/or organometallic salts.

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Tertiary amine catalysts generally have a strong odor and many are highly volatile due to their low molecular weight. The release of the tertiary amine during foam processing may present safety and toxicity concerns and the release of residual amine during customer handling is undesirable. The release of tertiary amine catalysts vapor in polyurethane products is also reported to be detrimental to vinyl film and polycarbonate sheets exposed thereto. Fugitive amines are also associated with fogging issues, that is, deposit of solids or liquid film on an automotive wind-shield.

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It is desirable to limit the volatility of this amine component or to lessen the amount of its use in a polyurethane formulation. In addition to reducing volatile organic compounds (VOC's), lessening volatility or reducing the level of amine use can reduce worker exposure, improve safety, and address quality concerns.

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Compounds with tertiary amine groups are known to be useful catalysts for urethane reactions. Certain polyols, sometimes referred to as autocatalytic polyols, contain tertiary amine groups which can reduce or eliminate the need for typical tertiary amine catalysts in formulations for polyurethanes while still maintaining the reactivity of the urethane reaction

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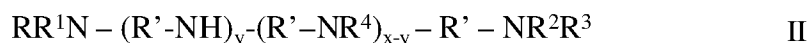
system. Further, the presence of multiple tertiary amine groups in such a polyol compound allows it to be chemically bound during a polyurethane gel or foam crosslinking reaction, for example. The resultant product can be substantially free of volatile amine emissions. However, many such autocatalytic polyols if used alone do not provide an optimal blowing:gelling ratio
 5 such that polyurethane polymers made therefrom may demonstrate inadequate processing, physical properties and/or mechanical properties. For example, see US Publication No. 2009/0227695 which suggests addition of traditional fugitive type amine catalysts may improve properties. However, such an approach leads to increased emission products.

Thus, for urethane applications, especially polyurethane foam applications, there
 10 remains a need to be able to produce polymeric polyol compounds from compositions having multiple tertiary amine groups which provide a good blowing:gelling ratio which provide good polyurethane processing, physical properties and mechanical properties in a polyurethane polymer produced therefrom while reducing, or eliminating, both the amount of fugitive tertiary amine catalyst used and the volatile amine emissions.

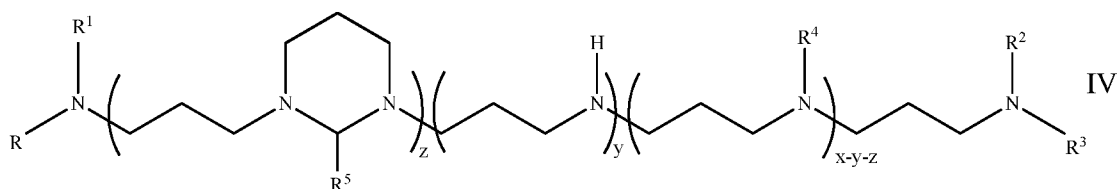
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SUMMARY OF THE INVENTION

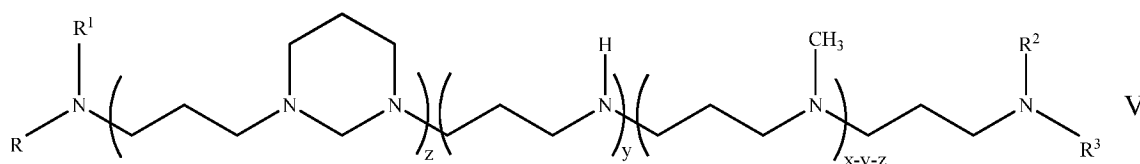
Accordingly, the present invention is directed to such a novel tertiary amine composition, initiator made therefrom, and polymeric polyol compositions made therefrom. The present invention is a polymeric amine composition comprising one or more amine compound represented by the Structure II:



wherein R' is a branched or linear C₁ to C₆ alkyl group, R, R¹, R², and R³ are independently a hydrogen or a C₁ to C₆ linear or branched alkyl group with the proviso that at least one of R, R¹, R², and R³ is not hydrogen, R⁴ is a hydrogen or a C₁ to C₆ linear or branched alkyl group, x is from 1 to 33, and y is from 0 to 32, with the proviso that that x-y is equal to or greater than 1 and the number of N-H bonds in (II) is greater than 0 and less than 8, preferably the one or more amine compound is represented by the Structure IV:



wherein R, R¹, R², and R³ are independently a hydrogen or a C₁ to C₆ linear or branched alkyl group with the proviso that at least one of R, R¹, R², and R³ is not hydrogen, R⁴ is a hydrogen or a C₁ to C₆ linear or branched alkyl group, R⁵ is a hydrogen or a C₁ to C₅ linear or branched alkyl group, x is from 1 to 33, y is from 0 to 32, and z is from 0 to 15, with the proviso that x-y-z is equal to or greater than 2 and the number of N-H bonds in (IV) is greater than 0 and less than 8, more preferably the one or more amine compound is represented by the Structure V:

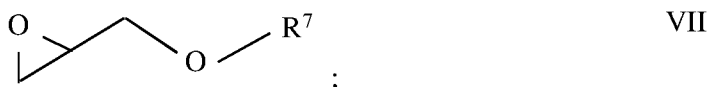


wherein R, R¹, R², and R³ are independently a hydrogen or a methyl group with the proviso that at least one of R, R¹, R², and R³ is not hydrogen, x is from 1 to 33, y is from 0 to 32, and z is from 0 to 15, with the proviso that that x-y-z is equal to or greater than 2 and the number of N-H bonds in (V) is greater than 0 and less than 8.

One embodiment of the present invention is a process to make a polymeric polyol composition comprising the reaction product(s) of: (i) the polymeric amine composition comprising one or more amine compound represented by the Structure II or Structure IV or Structure V described herein above and (ii) at least one epoxide compound having the structure VI:



or at least one glycidyl ether compound having the structure VII:



or a combination thereof; wherein R⁶ is hydrogen, phenyl, cyclohexyl, or a C₁-C₁₈ linear or branched alkyl and R⁷ is hydrogen, phenyl, a C₁ to C₆ linear or branched alkyl-substituted phenyl, or a C₁ to C₁₈ linear or branched alkyl.

One embodiment of the present invention is a process to make a polyurethane polymer by reaction of a mixture comprising: (A) a polymeric polyol formulation comprising the polymeric polyol composition described herein above, (B) at least one organic isocyanate, (C) optionally a blowing agent, and (D) optionally additives or auxiliary agents known per se for the production of polyurethane polymers.

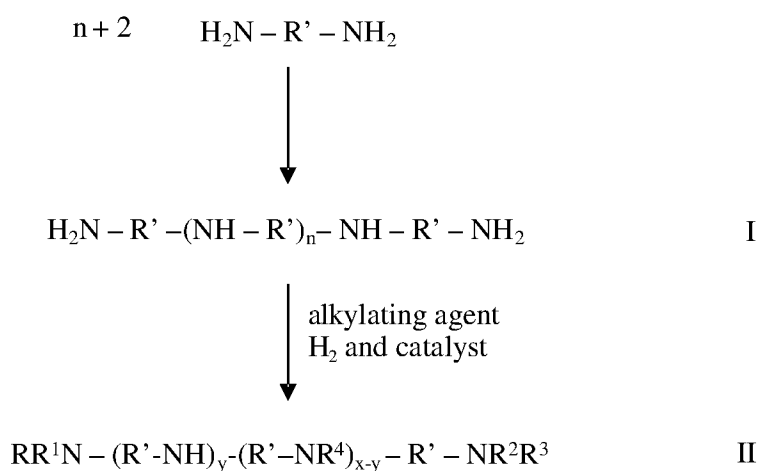
Another embodiment of the present invention is the process described herein above wherein the reaction occurs in the presence of a blowing agent and the polyurethane polymer is produced in the form of a polyurethane flexible foam.

DETAILED DESCRIPTION OF THE INVENTION

The present invention discloses a novel partially alkylated polyamine initiator composition, herein after referred to as a tertiary amine composition, for the production of polyether polyols and polyurethane polymers made therefrom.

Generally, the alkylated polyamine composition of the present invention can be made as shown in Scheme 1.

Scheme 1



wherein R' is a branched or linear C₁ to C₆ alkyl group,

R, R¹, R², and R³ are independently a hydrogen or a C₁ to C₆ linear or branched alkyl group with the proviso that at least one of R, R¹, R², and R³ is not hydrogen,

R⁴ is a hydrogen or a C₁ to C₆ linear or branched alkyl group,

x is from 1 to 33,

and

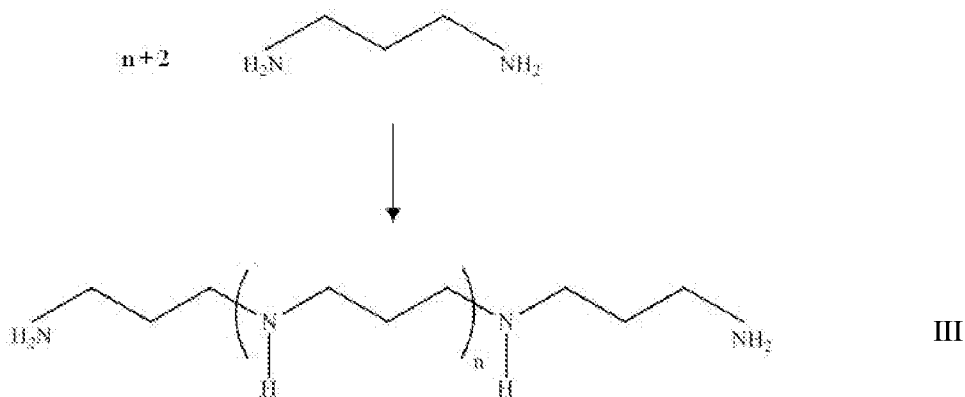
y is from 0 to 32,

with the proviso that that x-y is equal to or greater than 1 and the number of N-H bonds in (II) is greater than 0 and less than 8.

In a preferred embodiment of the present invention, the alkylated polyamine composition can be made as shown in Schemes 2 and 3. The first step is to polymerize a polyamine compound such as 1, 3-diamine propane (1, 3-DAP) to form a polyamine represented by Structure III.

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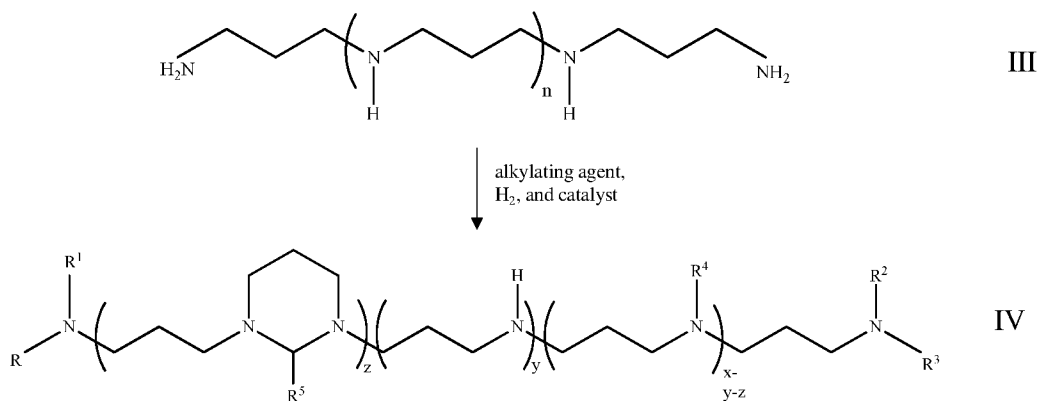
Scheme 2



The second step is to alkylate the polyamine with an alkylating agent, preferably formaldehyde, to form a mixture of alkylated polyamine products. For example the reaction of polymeric 1, 3-DAP with an alkylating agent, may yield a mixture of products represented by Structure IV:

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Scheme 3



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wherein R, R¹, R², and R³ are independently a hydrogen or a C₁ to C₆ linear or branched alkyl group with the proviso that at least one of R, R¹, R², and R³ is not hydrogen,

R⁴ is a hydrogen or a C₁ to C₆ linear or branched alkyl group,

R⁵ is a hydrogen or a C₁ to C₅ linear or branched alkyl group,

x is from 1 to 33,

y is from 0 to 32,

and

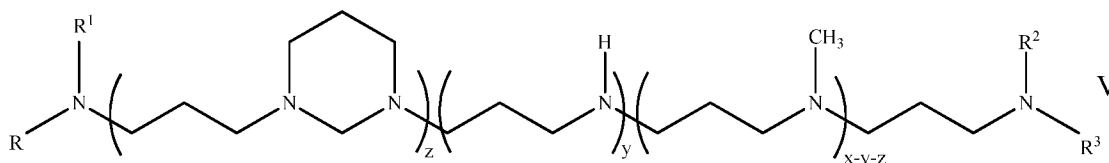
z is from 0 to 15,

with the proviso that that x-y-z is equal to or greater than 2 and the number of N-H bonds in (IV) is greater than 0 and less than 8.

In addition to the reaction product(s) of the polyamine and alkylating agent the mixture may further comprise some unreacted polyamine.

In one embodiment, the alkylating agent is formaldehyde and the resulting alkylated polyamine is represented by Structure V:

5



wherein R, R¹, R², and R³ are independently a hydrogen or a methyl group with the proviso that at least one of R, R¹, R², and R³ is not hydrogen,

x is from 1 to 33,

y is from 0 to 32,

and

z is from 0 to 15,

with the proviso that that x-y-z is equal to or greater than 2 and the number of N-H bonds in (V) is greater than 0 and less than 8.

Methods to make polyamines are known, for example see USP 9,000,217 and US Publication No. 2013/0231476, each is incorporated herein by reference in its entirety. The polyamine of the present invention is made by subjecting a diamine compound that has at least two non-tertiary amine groups that are separated from one another by a ternary or greater carbon spacing (C₃ or greater spacing) to a transamination reaction in the presence of a hydrogen/dehydrogenation catalyst to obtain a mixture of linear high molecular weight polyamine compounds having one or more nitrogen atoms (Scheme 1). To a minor extent, branched and/or cyclic high molecular weight polyamine compounds may be produced as well. Examples of suitable diamine compounds include 1,3-diaminopropane (1,3-DAP), 1,3-

pentanediamine; 1,3-butanediamine; 2,2-dimethyl-1,3-propanediamine; 2,2-diethyl-1,3-propanediamine; 1,3-diamino-2-phenylpropane; 2-(aminomethyl)-2-methyl-1,3-propanediamine; combinations of these, and the like, 1,3-DAP is most preferred. Adjustment of reaction conditions can customize the product mixture. Examples of other reaction conditions that can be used to customize product compositions include the nature of the catalyst, the concentration of catalyst on its carrier in the case of heterogeneous catalysts, the physical form of the catalyst, the pressure of the reaction, the concentration of H₂ during the reaction, conversion, temperature, combinations of these, and/or the like.

Transamination may be carried out in a variety of ways. In accordance with a preferred mode of practice, the reactants are combined and caused to react in a suitable reactor volume in the presence of a suitable catalyst under temperature and pressure conditions effective to cause the transamination reaction.

The methods of the invention can be practiced in any suitable reactor. These include batch reactors, continuous fixed bed reactors, slurry bed reactors, fluidized bed reactors, catalytic distillation reactors, combinations of these, and the like.

The catalyst material employed in the present invention comprises hydrogenation/dehydrogenation catalysts. Useful catalysts are those based upon nickel (such as Raney nickel and Urushibara nickel), rhenium, cobalt, copper, and mixtures thereof. Particularly useful catalysts comprise nickel/rhenium and nickel/cobalt. A most preferred catalyst comprises nickel (Ni) and rhenium (Re). In preferred embodiments in which a heterogeneous catalyst incorporates nickel and rhenium, useful supports are comprised of alumina-silica particles. Such catalysts and methods of making such heterogeneous catalysts on such supports are further described in USP 8,293,676; 8,187,997; and 6,534,441, each is incorporated herein by reference in its entirety.

The catalysts can be heterogeneous, homogeneous, or a combination of these may be used. Heterogeneous catalysts are preferred. Often, heterogeneous catalysts comprise one or more catalytic materials supported upon a suitable substrate. The substrate may be used in various shapes or combinations such as, for example, powder, particle, pellet, granule, extrudate, fiber, shell, honeycomb, plate, or the like. The particles can be regular in shape, irregular, dendritic, dendrite-free, or the like. Preferred supports are particulate in nature or powders. Suitable supports in the practice of the present invention include carbonaceous materials, siliceous materials (such as silica), metal compounds such as metal oxides, combinations of these, and the like. Representative metal oxides include oxides of one or more of magnesium, aluminum, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, gallium, germanium, strontium, yttrium, zirconium, niobium, molybdenum,

technetium, ruthenium, rhodium, palladium, silver, cadmium, indium, iron, tin, antimony, barium, lanthanum, hafnium, thallium, tungsten, rhenium, osmium, iridium, and platinum.

The amount of catalyst used in forming a high molecular weight polyamine using transamination is any amount which is effective in producing the desired acyclic polyamine. For batch conditions, the quantity of catalyst may be in the range from about 0.1 to about 20 weight percent, preferably 1 to 15 weight percent, of catalyst per 100 parts by weight of reactant(s) to form the desired triamine. In a continuous process, a typical strategy might involve causing a flow of reactants to contact a bed of heterogeneous catalyst particles. In such a case, the space velocity (usually expressed in units of gmol/ (kg catalyst/hr) can be adjusted to balance factors such as production and selectivity.

The reaction mixture for transamination can be contacted with catalyst at any suitable temperature(s) that produce the desired acyclic polyamine. Typically, the temperature is maintained below about 350°C, preferably below 300°C. Preferred temperatures are in the range from about 130°C to about 200°C for transamination. Below the preferred temperature ranges, the conversion to acyclic polyamine may be too slow to be practical for commercial scale production. Above the preferred temperature ranges, selectivity may be reduced to an undue degree, increasing the yield of by-products. In some instances, such by-products may have commercial value and be desirable as a consequence. In other instances, by-products constitute impurities as a practical matter.

Similarly, the reaction mixture for transamination can be contacted with catalyst at any suitable pressure(s) that promotes the reaction to produce the desired high molecular weight polyamine. Preferably, the pressure is sufficient to maintain the reactor contents in a liquid state as the reaction proceeds. In many instances, the pressure will vary as the reaction proceeds. For instance, ammonia is a by-product of a typical transamination process. The production of ammonia causes the pressure generally to increase as the reaction proceeds in pressure sealed reactors. Ammonia and/or other pressure-increasing products can be removed from the reactor in order to keep the pressure below a desired threshold. Typically, the pressure is at least 200 psi, preferably at least 1000 psi, and preferably less than 1500 psi. Within these guidelines, the pressure is typically in the range from about 100 psi to 1500 psi, preferably 200 psi to 1500 psi, more preferably 300 psi to 1000 psi. For transamination, pressures in the range of 400 psi to about 1000 psi are preferred.

Catalytic reductive N-alkylation of amines to produce tertiary amines is well known, for example see Underwood, Richard P. and Carr, Richard V. C., *Reaction Pathways in the Catalytic Reductive N-Methylation of Polyamines*, Chemical Industries (Dekker), 82, (Catalysis of Organic Reactions), 267 (2001); GB 1,305,258; and USP 5,105,013 which is incorporated

herein by reference in its entirety. Catalytic reductive N-alkylation is typically carried out by reacting a primary or secondary amine with a C₁ to C₆ linear or branched alkyl aldehyde, preferably the alkyl aldehyde is C₁ or formaldehyde, and hydrogen in the presence of a metal catalyst, preferably Pd, Pt, or Ni (Scheme 3).

The term formaldehyde as used herein is intended to include within its scope both formaldehyde itself, and substances capable of decomposing to provide formaldehyde under the reaction conditions employed, for example trioxane and para-formaldehyde. The formaldehyde may be aqueous formalin or a formaldehyde solution in methanol. The formaldehyde concentration may be from about 30 to about 60 percent. Preferably, about 35 to about 37 percent aqueous formalin is used. The quantity of formaldehyde that is used is less than equimolar quantity as compared to the amount of reactive hydrogens on the amines. In order to prepare the Structure V it is critical to leave unreacted NH or NH₂ functionality that are available for the next step of alkoxylation with the oxides (i.e. propylene oxide) and subsequent growth of the polyether to produce the desired polyamine centroid active polyols, preferably the number of residual N-H bonds in (V) is greater than 0 and less than 8. The amount of formaldehyde is determined by the total number of moles of NH groups in Structure I and then adding only enough formaldehyde to react less than 100% of them.

The reaction is carried out in the presence of a reductive methylation catalyst, many of which are known. Such catalysts generally comprise Ni, Pd, Co, Pt, or Cu. In the process of this invention, the preferred catalysts are those comprising nickel, cobalt or copper, and most preferred are nickel catalysts such as Raney Nickel. They may be employed as fixed bed catalysts or used in powdered form, whichever is convenient for the reactor and equipment available. In one embodiment, nickel catalysts are those which are activated by relatively low temperatures, for example 25°C to 120°C.

The ratio of catalyst to amine will generally depend on the nature of the amine, its molecular weight and the catalyst employed, but is preferably within the range of about 0.1 to about 30 g, more preferably about 4.0 to about 8.0 g of catalyst/mole of amine. A lower catalyst concentration tends to reduce the hydrogenation rate to unacceptable levels, and thus lower the conversion. Higher catalyst concentrations increase the rate of hydrogenolysis, but tend to result in an increase in temperature, which results in unwanted side-reactions being favored, and thus an increased production of by-products.

The reaction is typically carried out at a temperature equal to or greater than 25°C, preferably equal to or greater than 50°C, and more preferably equal to or greater than 75°C. The reaction is typically carried out at a temperature equal to or less than 150°C, preferably equal to or less than 120°C, and more preferably equal to or less than 100°C.

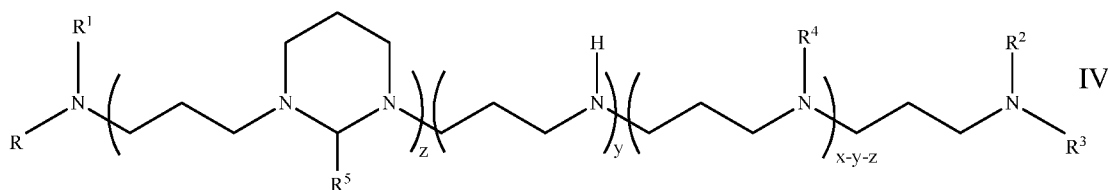
The reaction is typically carried out at a pressure of equal to or greater than 1 bar, preferably equal to or greater than 2 bar, and more preferably equal to or greater than 5 bar. The reaction is typically carried out at a pressure of equal to or less than 50 bar, preferably equal to or less than 20 bar, and more preferably equal to or less than 10 bar.

In one embodiment the reaction is carried out in two steps, in the first step the formaldehyde is added at a lower temperature and pressure, for example 10°C to 50°C and 1 to 2 bar, and in the second step the hydrogenation is done at a higher temperature and pressure, for example 100°C to 150°C and 30 to 70 bar.

It is particularly preferred in the method of the invention that the reaction is carried out in the presence of a volatile organic solvent. The volatile organic solvent should be one in which all the reactants are soluble and one which can readily be removed from the mixture at the end of the reductive methylation reaction. Suitable solvents are those having a boiling point of about 120°C or less and include aliphatic alcohols. Especially preferred are the aliphatic primary alcohols which include, for example, methanol, ethanol, propan-1-ol, n-butanol, or mixtures thereof. Such solvents are preferred, because of the relatively high solubility of hydrogen in them, as compared with water.

The ratio of the volatile organic solvent to the amine is preferably 0.75:1 to 1.5:1 by weight, more preferably from 1.0:1 to 1.4:1 by weight, most preferably about 1.2:1. The use of a volatile solvent enables the solvent to be readily removed by volatilization, to enable the product to be recovered.

The partially alkylated amine compounds prepared comprise a mixture of primary and secondary and tertiary amines and linear and cyclic alkylated polyamines. For example, when polymeric 1, 3-DAP is alkylated the product is represented by Structure IV:



wherein R, R¹, R², and R³ are independently a hydrogen or a C₁ to C₆ linear or branched alkyl group, preferably C₁, with the proviso that at least one of R, R¹, R², and R³ is not hydrogen,

R⁴ is a hydrogen or a C₁ to C₆ linear or branched alkyl group, preferably C₁,

R⁵ is a hydrogen or a C₁ to C₅ linear or branched alkyl group, preferably H,

x is from 1 to 33,

y is from 0 to 32,

and

z is from 0 to 15,

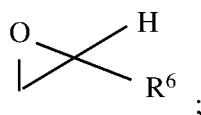
with the proviso that x-y-z is equal to or greater than 2 and the number of N-H bonds in (IV) is greater than 0 and less than 8.

The resulting partially alkylated polyamine compound is suitable for use as a partially alkylated polyamine initiator composition of the present invention. Said partially alkylated polyamine initiator composition may be used to prepare polymeric polyol compositions comprising polyol compounds. The partially alkylated polyamine initiator composition may be used as produced to prepare a polymeric polyol composition, in other words, without any purification or isolation of specific reaction products and/or recovery of unreacted starting materials (e.g., polyamine and/or alkylating agent). Alternatively, unreacted starting materials may be removed from the partially alkylated polyamine initiator composition, and/or specific reaction products may be isolated from the reaction product mixture. If specific reaction products are desired, they may be isolated and/or further purified, for example by distillation or extraction.

The partially alkylated polyamine initiator composition of the present invention preferably has an average weight average molecular weight (Mw) equal to or less than 5,000, preferably equal to or less than 2,500, more preferably equal to or less than 1,000, and even more preferably equal to or less than 500. The above initiator composition preferably has a Mw
5 equal to or greater than 100, preferably equal to or greater than 200, and more preferably equal to or greater than 300. The Mw data in accordance with this disclosure can be determined by Gel Permeation Chromatography.

The above initiator composition preferably has an average hydroxyl number (reported as mg KOH/g) equal to or greater than 30, preferably equal to or greater than 40, more preferably
10 equal to or greater than 50, and even more preferably equal to or greater than 60. The above initiator composition preferably has an average hydroxyl number equal to or less than 90, preferably equal to or less than 80, and more preferably equal to or less than 70. The hydroxyl number is measured by ASTM D4274 D.

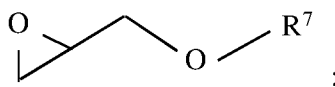
The partially alkylated polyamine initiator composition is useful to produce a novel
15 polymeric polyol composition comprising polymeric polyol compounds. A first polymeric polymer composition is the reaction product(s) of an initiator composition as described herein above with at least one epoxide compound having the structure VI:



VI

or

at least one glycidyl ether compound having the structure VII:



VII

5

or a combination thereof;

wherein R⁶ is hydrogen, phenyl, cyclohexyl, or a C₁–C₁₈ linear or branched alkyl

and

10 R⁷ is hydrogen, phenyl, a C₁ to C₆ linear or branched alkyl-substituted phenyl, or a C₁ to C₁₈ linear or branched alkyl.

In structure VI, R⁶ can be hydrogen, phenyl, cyclohexyl, or a C₁–C₁₈ linear or branched alkyl. In accordance with one aspect of the present invention, R⁶ is methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, 2-ethylhexyl, octyl, decyl, dodecyl, tetradecyl, hexadecyl, or octadecyl. In
 15 another aspect, R⁶ can be hydrogen, phenyl, or cyclohexyl. In yet another aspect, R⁶ is hydrogen, methyl, or phenyl. In this aspect, where R⁶ is hydrogen, methyl, butyl, or phenyl, the epoxide compounds of structure VI are, respectively, ethylene oxide, propylene oxide, butylene oxide, or styrene oxide.

In structure VII, R⁷ can be hydrogen, phenyl, a C₁ to C₆ linear or branched alkyl-
 20 substituted phenyl, or a C₁ to C₁₈ linear or branched alkyl. For instance, R⁷ can be hydrogen, phenyl, or a C₁ to C₆ linear or branched alkyl-substituted phenyl, in one aspect of this invention. R⁷ is methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, 2-ethylhexyl, octyl, decyl, dodecyl, tetradecyl, hexadecyl, or octadecyl, in another aspect of this invention. Yet, R⁷ can be phenyl or butyl-substituted phenyl in still another aspect of this invention.

25 The above resulting polymeric polyol composition preferably has a Mw equal to or less than 10,000, preferably equal to or less than 8,000, and even more preferably equal to or less than 6,000. The above resulting polymeric polyol composition preferably have a Mw equal to or greater than 500, preferably equal to or greater than 2,500, and more preferably equal to or greater than 5,000.

30 According to one aspect of the present invention, the polymeric polyol composition disclosed herein above has a hydroxyl number of equal to or less than 90 mg KOH/g, preferably

equal to or less than 80, more preferably equal to or less than 70, more preferably equal to or less than 60, and even more preferably equal to or less than 50 mg KOH/g. The resulting polymeric polyol composition disclosed herein above have a hydroxyl number equal to or greater than 20 mg KOH/g, preferably equal to or greater than 30, more preferably equal to or greater than 40 mg KOH/g. Hydroxyl number is determined according to ASTM D 4274.

In another aspect of the present invention, the herein above polymeric polyol composition has an average functionality (F) equal to or less than 12, preferably equal to or less than 10, more preferably equal to or less than 8, more preferably equal to or less than 6, and even more preferably equal to or less than 4. Preferably, the above polymeric polyol composition has an average functionality equal to or greater than 1, and more preferably equal to or greater than 3.

The polymeric polyol compositions of this invention also can be characterized by nitrogen content. For instance, amine values of polymeric polyol compositions disclosed herein above are equal to or less than 3 mg/g KOH/g, preferably equal to or less than 2, more preferably equal to or less than 1, more preferably equal to or less than 0.5 mg KOH/g. Nitrogen content is determined according to ASTM D 6979 and reported as percent Nitrogen.

Making polymeric polyol compositions is well known in the art; any suitable process to make polymeric polyol compositions from initiator II above is acceptable. For instance, initiator II can be mixed with a catalyst and this mixture is subsequently reacted with ethylene oxide or propylene oxide at a temperature in a range from about 100°C to 160°C. A traditional catalyst used in this reaction, and known to those of skill in the art, is KOH. Other alkaline hydroxide or hydroxide hydrate catalysts based on Ba (barium) or Sr (strontium) can be employed as the alkoxylation catalyst; producing products with less unsaturation than those produced using the traditional KOH catalyst. Processes for producing polyols using Ba or Sr catalysts are described in USP 5,070,125; 5,010,187; and 5,114,619, the disclosures of which are incorporated by reference in their entirety. High levels of unsaturation, especially with polyols of high equivalent weight, act as chain terminators in polyurethane foam production, giving rise to, for example, foams with poor compressive strength, poor tensile strength, reduced reactivity, and reduced aging performance under humid conditions. The Ba and Sr catalysts also provide improved primary hydroxyl capping efficiency for the same weight percentage of ethylene oxide used. When using Ba or Sr catalysts, water can be added during the reaction of the ethylene oxide or propylene oxide with the initiator. This water addition can reduce the amount of unsaturation in the final polyol product. Another catalyst that can be used to produce polyols is a double metal cyanide (DMC) catalyst, which may provide a different molecular weight distribution of the polymeric polyol composition from that achieved using

KOH. Examples of double metal cyanide catalysts are provided in USP 5,470,813; 5,589,431; and 6,008,263, the disclosures of which are incorporated herein by reference in their entirety.

We have found that a polymeric polyol composition comprising one or more polymeric polyol composition based on the partially alkylated polyamine initiator composition of the present invention is particularly useful for making polyurethane polymers, especially polyurethane foam polymers having good processing, good mechanical properties, good physical properties, and having low emission products. Further, we have found that a polymeric polyol formulation comprising one or more first polymeric polyol composition based on the partially alkylated polyamine initiator composition of the present invention and one or more additional polymeric polyol composition based on a second initiator, different from the first polyol composition based on the partially alkylated polyamine initiator composition of the present invention, is particularly useful for making polyurethane polymers, especially polyurethane foam polymers having good mechanical properties, good physical properties, and having low emission products.

In a polyol formulation, wherein more than one polymeric polyol composition is used, the weight ratio of the first polymeric polyol composition to the at least one second polyol can range from 50:1 to 1:5,000. In other aspects, the weight ratio of the first polymeric polyol composition to the at least one second polyol in the polyol formulation can range from 10:1 to 1:1,000, from 5:1 to 1:500, or from 4:1 to 1:250. Yet, in other aspect, the weight ratio of the first polymeric polyol composition to the at least one second polyol is in a range from 3:1 to 1:100, or from 2:1 to 1:50.

While compositions and methods are described in terms of "comprising" various components or steps, the compositions and methods can also "consist essentially of" or "consist of" the various components or steps.

Generally, polyurethane foam catalyst systems comprise compounds which accelerate both the blowing (water-isocyanate) and gelling (polyol-isocyanate) reactions. It is beneficial to balance these reactions in order to produce quality foams with acceptable properties. Compositions and formulations of the present invention can comprise a single compound which accelerates, but keeps in balance, both the blowing and gelling reactions. Alternatively, the compositions can comprise at least one catalyst that predominantly accelerates the blowing reaction (a blowing catalyst), or at least one catalyst that predominantly accelerates the gelling reaction (a gelling catalyst), or a combination thereof. As described herein, a blowing catalyst is a catalyst that predominantly accelerates the blowing reaction, but can also, in certain circumstances, accelerate the gelling reaction, albeit to a lesser degree. Similarly, a gelling catalyst is a catalyst that predominantly accelerates the gelling reaction, but can also, in certain

circumstances, accelerate the blowing reaction, albeit to a lesser degree. Surprisingly, we have found that a polymeric polyol formulation comprising one or more polymeric polyol composition based on the partially alkylated polyamine initiator composition of the present invention provides a good blowing:gelling ratio such that polyurethane polymers made from said mixture of polymeric polyols, especially polyurethane foam polymers, have very good mechanical properties and physical properties and demonstrate low levels of emission products.

The presence of multiple tertiary amine groups in the polymeric polyol compositions of the present invention can either reduce or eliminate the need to include a conventional fugitive urethane catalyst when formulating a polyurethane polymer or polyurethane polymer foam. However, in other aspects of the present invention, conventional urethane catalysts can be employed in compositions or formulations along with such polymeric polyol compositions.

In addition to the polymeric polyol compositions disclosed herein above, one or more additional polyol may be used in the polymeric polyol formulation for use in making a polyurethane polymer of the invention. As used herein the term polyols are those materials having at least one group containing an active hydrogen atom capable of undergoing reaction with an isocyanate. Preferred among such compounds are materials having at least two hydroxyls, primary or secondary, or at least two amines, primary or secondary, carboxylic acid, or thiol groups per molecule. Compounds having at least two hydroxyl groups or at least two amine groups per molecule are especially preferred due to their desirable reactivity with polyisocyanates.

Suitable polyols that may be used to produce polyurethane foams of the present invention are well known in the art and include those described herein and any other commercially available polyol and/or SAN, PIPA or PHD copolymer polyols. Such polyols are described in "Polyurethane Handbook", by G. Oertel, Hanser publishers. Mixtures of one or more polyols and/or one or more copolymer polyols may also be used to produce polyurethane products according to the present invention.

Representative polyols include polyether polyols, polyester polyols, polyhydroxy-terminated acetal resins, hydroxyl-terminated amines and polyamines. Natural oil based polyols can also be used. Examples of these and other suitable isocyanate-reactive materials are described more fully in USP 4,394,491. Alternative polyols that may be used include polyalkylene carbonate-based polyols and polyphosphate-based polyols. Preferred are polyols prepared by adding an alkylene oxide, such as ethylene oxide, propylene oxide, butylene oxide or a combination thereof, to an initiator or blend of initiators to give a final polyol a nominal functionality having from 2 to 8, preferably 2 to 6 active more preferably 2.1 to 4 active hydrogen atoms. Catalysis for this polymerization can be either anionic or cationic, with

catalysts such as KOH, CsOH, boron trifluoride, or a double metal cyanide complex (DMC) catalyst such as zinc hexacyanocobaltate, or quaternary phosphazanium compounds. In the case of alkaline catalysts, these are eliminated from the polyol at the end of production by a proper finishing step, such as coalescence, magnesium silicate (magsil) separation, ion exchange or less preferably by acid neutralization. In the case of DMC catalyst produced polyols, the finishing step can be avoided.

The polyols or blends thereof employed depend upon the end use of the polyurethane foam to be produced. The hydroxyl number and molecular weight of the polyol or polyols employed can vary accordingly over a wide range. In general, the hydroxyl number of the polyols employed for use in producing a flexible or visco-elastic foam may range from 15 to 300.

In the production of a flexible polyurethane foam, the polyol is preferably a polyether polyol and/or a polyester polyol or a polyetherester polyol. The polyol generally has an average functionality ranging from 2 to 5, preferably 2 to 4, and an average hydroxyl number ranging from 15 to 300 mg KOH/g, preferably from 20 to 200, and more preferably from 20 to 70mg KOH/g. As a further refinement, the specific foam application will likewise influence the choice of base polyol. As an example, for molded foam, the hydroxyl number of the base polyol may be on the order of 20 to 60 with ethylene oxide (EO) capping, and for slabstock foams the hydroxyl number may be on the order of 25 to 75 and is either mixed feed EO/PO (propylene oxide) or is only slightly capped with EO or is 100 percent PO based.

In the production of a visco-elastic foam, polyols having a functionality as for flexible foam can be used, however; the polyol or polyol blend will preferably contain polyols having a hydroxyl number from 150 to 300 mg KOH/g. For the production of semi-rigid foams or microcellular elastomers, it is preferred to use a trifunctional polyol with a hydroxyl number of 30 to 80.

The isocyanates which may be used in the present invention include aliphatic, cycloaliphatic, arylaliphatic and aromatic isocyanates. For the production of slabstock foam, aromatic isocyanates are preferred.

Examples of suitable aromatic isocyanates include the 4,4'-, 2,4' and 2,2'-isomers of diphenylmethane diisocyanate (MDI), blends thereof and polymeric and monomeric MDI blends toluene-2,4- and 2,6-diisocyanates (TDI), m- and p-phenylenediisocyanate, chlorophenylene-2,4-diisocyanate, diphenylene-4,4'-diisocyanate, 4,4'-diisocyanate-3,3'-dimehtyldiphenyl, 3-methyldiphenyl-methane-4,4'-diisocyanate and diphenyletherdiisocyanate and 2,4,6-triisocyanatotoluene and 2,4,4'-triisocyanatodiphenylether.

Mixtures of isocyanates may be used, such as the commercially available mixtures of 2,4- and 2,6-isomers of toluene diisocyanates. A crude polyisocyanate may also be used in the practice of this invention, such as crude toluene diisocyanate obtained by the phosgenation of a mixture of toluene diamine or the crude diphenylmethane diisocyanate obtained by the phosgenation of crude methylene diphenylamine. TDI/MDI blends may also be used. MDI or TDI based prepolymers can also be used, made either with a polymeric polyol composition comprising initiator (I) and/or , a polymeric polyol composition comprising initiator (XII) or any other polyol as described heretofore. Isocyanate-terminated prepolymers are prepared by reacting an excess of polyisocyanate with polyols, including aminated polyols or imines/enamines thereof, or polyamines.

Examples of aliphatic polyisocyanates include ethylene diisocyanate, 1,6-hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI), cyclohexane 1,4-diisocyanate, 4,4'-dicyclohexylmethane diisocyanate (H₁₂MDI), saturated analogues of the above mentioned aromatic isocyanates and mixtures thereof.

For the production of flexible foams, the preferred polyisocyanates are the toluene-2,4- and 2,6-diisocyanates or MDI or combinations of TDI/MDI or prepolymers made therefrom.

For producing a polyurethane-based foam, a blowing agent is generally required. In the production of flexible polyurethane foams, water is preferred as the blowing agent. The amount of water is preferably in the range of from 0.5 to 10 parts by weight, more preferably from 2 to 7 parts by weight based on 100 parts by weight of the polyol and even more preferably the water is between 2 and 5 parts per hundred parts polyol. In some applications the water is preferably present in 3 parts by weight of the polyol. In some preferred embodiment, the water is present at of 6 parts or less by weight of the polyol. When water is present at less than 3 parts, a small conventional amine catalyst can be used to enhance the reactivity of the system. The amount of conventional amine catalyst included in such formulations is generally from 0.01 to 0.1 weight percent of the polyol. To further reduce the level of volatile amine, such a catalyst is used as less than 0.05 weight percent of the polyol. Although not preferred, other blowing agents can be liquid or gaseous carbon dioxide, methylene chloride, acetone, pentane, isopentane, cyclopentane, methylal or dimethoxymethane, dimethylcarbonate. Use of artificially reduced, or increased, atmospheric pressure, such as disclosed in US 5,194,453, or frothing, can also be contemplated with the present invention.

In addition to the foregoing critical components, it is often desirable to employ certain other ingredients in preparing polyurethane polymers. Among these additional ingredients are

catalysts, surfactants, preservatives, flame retardants, colorants, antioxidants, reinforcing agents, stabilizers and fillers, recycled polyurethane powder.

One or more catalysts for the reaction of the polyol with the polyisocyanate can be used. Any suitable urethane catalyst may be used, including tertiary amine compounds, amines with isocyanate reactive groups and organometallic compounds. Preferably the reaction is carried out in the absence of an amine or an organometallic catalyst or a reduced amount as described above. Exemplary tertiary amine catalysts include triethylenediamine; N-methylmorpholine; N,N-dimethylcyclohexylamine; pentamethyldiethylenetriamine; tetramethylethylenediamine; bis (dimethylaminoethyl)ether; N-ethylmorpholine; dimethylethanolamine; N-cocomorpholine; 1-methyl-4-dimethylaminoethyl-piperazine; 3-methoxy-N-dimethylpropylamine; N,N-dimethyl-N',N'-dimethyl isopropylpropylenediamine; N,N-diethyl-3-diethylamino-propylamine and dimethylbenzylamine. Exemplary organometallic catalysts include organomercury, organolead, organoferriic and organotin catalysts, with organotin catalysts being preferred among these. Suitable tin catalysts include stannous chloride, tin salts of carboxylic acids such as dibutyltin di-laurate, and stannous octoate, as well as other organometallic compounds such as are disclosed in U.S. Patent 2,846,408. A catalyst for the trimerization of polyisocyanates, resulting in a polyisocyanurate, such as an alkali metal alkoxide may also optionally be employed herein. The amount of amine catalysts can vary from 0.02 to 5 percent in the formulation or organometallic catalysts from 0.001 to 1 percent in the formulation can be used.

In one preferred embodiment of the present invention, the foams are produced with a catalyst package that includes a tin catalyst. Preferably such formulations do not contain a conventional amine catalyst.

In making polyurethane foam, it is generally preferred to employ an amount of a surfactant to stabilize the foaming reaction mixture until it cures. Such surfactants advantageously comprise a liquid or solid organosilicone surfactant. Other surfactants include polyethylene glycol ethers of long-chain alcohols, tertiary amine or alkanolamine salts of long-chain alkyl acid sulfate esters, alkyl sulfonic esters and alkyl arylsulfonic acids. Such surfactants are employed in amounts sufficient to stabilize the foaming reaction mixture against collapse and the formation of large, uneven cells. Typically, 0.2 to 3 parts of the surfactant per 100 parts by weight total polyol (b) are sufficient for this purpose.

A crosslinking agent or a chain extender may be added, if necessary. The crosslinking agent or the chain extender includes low-molecular weight polyhydric alcohols such as ethylene glycol, diethylene glycol, 1,4-butanediol, and glycerin; low-molecular weight amine polyol such as diethanolamine and triethanolamine; polyamines such as ethylenediamine, xlylenediamine,

and methylene-bis(o-chloroaniline). The use of such crosslinking agents or chain extenders is known in the art as disclosed in U.S. Patents 4,863,979, 4,883,825 and 4,963,399 and EP 549,120.

When preparing foams for use in transportation, a flame retardant is sometimes included
5 as an additive. Any known liquid or solid flame retardant can be used with the autocatalytic polyols of the present invention. Generally such flame retardant agents are halogen-substituted phosphates and inorganic flame proofing agents. Common halogen-substituted phosphates are tricresyl phosphate, tris(1,3-dichloropropyl phosphate, tris(2,3-dibromopropyl) phosphate and tetrakis (2-chloroethyl)ethylene diphosphate. Inorganic flame retardants include red
10 phosphorous, aluminum oxide hydrate, antimony trioxide, ammonium sulfate, expandable graphite, urea or melamine cyanurate or mixtures of at least two flame retardants. In general, when present, flame retardants are added at a level of from 5 to 50 parts by weight, preferable from 5 to 25 parts by weight of the flame retardant per 100 parts per weight of the total polyol present.

The particular polyol, polyol mixture, and polyol amount used in the polyurethane foam
15 forming composition can be chosen based on the factors such as the desired polyurethane foam properties and/or the particular end use of the foam product. Properties of the polyol such as molecular weight or hydroxyl number can be chosen to provide foam characteristics selected from: low density, high density foam, conventional, high resilient, hot molding, cold molding,
20 flexible, and rigid, and desired combinations thereof. For many applications or foam properties, the hydroxyl number of the polyol is in the range of about 15 to about 800.

Compositions for the production of flexible polyurethane foams typically include a polyether polyol and/or a polyester polyol. The polyol generally has an average functionality ranging from 2 to 5, preferably 2 to 4, and an average hydroxyl number ranging from 20 to 100
25 mg KOH/g, preferably from 20 to 75 mgKOH/g (see, for example, USP 7,361,695 which is incorporated herein by reference in its entirety).

For molded foam, the hydroxyl number of the base polyol can be in the range of about 20 to about 60 with ethylene oxide (EO) capping, and for slabstock foams the hydroxyl number can be in the range of about 25 to about 75 (see, for example, USP 7,361,695 which is
30 incorporated herein by reference in its entirety).

Processes for producing polyurethane foam products are well known in the art. In general components of the polyurethane-forming reaction mixture can be mixed together in any convenient manner, for example by using any of the mixing equipment described in the prior art such as in Polyurethane Handbook, by G. Oertel, Hanser publisher.

The polyurethane products can be produced continuously or discontinuously, by injection, pouring, spraying, casting, calendering, etc. Foams can be made under free rise or molded conditions, at atmospheric pressure, reduced or increased air pressure, with or without release agents, in-mold coating, or with any inserts or skin put in the mold. Flexible molded
5 foams can be mono- or dual-hardness.

For example, a polyurethane polymer of the present invention may be made by the reaction of a mixture comprising: a polymeric polyol formulation comprising: a polymeric polyol composition comprising initiator II; at least one organic isocyanate; optionally a blowing agent; and optionally additives or auxiliary agents known per se for the production of
10 polyurethane polymers for example, catalysts, surfactants, preservatives, flame retardants, colorants, antioxidants, reinforcing agents, stabilizers, fillers, and recycled polyurethane powder .

Slabstock foam is conveniently prepared by mixing the foam ingredients and dispensing them into a trough or other region where the reaction mixture reacts, rises freely against the
15 atmosphere (sometimes under a film or other flexible covering) and cures. In common commercial scale slabstock foam production, the foam ingredients (or various mixtures thereof) are pumped independently to a mixing head where they are mixed and dispensed onto a conveyor that is lined with paper or plastic. Foaming and curing occurs on the conveyor to form a foam bun. The resulting foams are typically from about from 10 kg/m³ to a maximum of
20 80 kg/m³. A preferred range is from 10 kg/m³ to 70 kg/m³ and more preferably from 10 kg/m³ to 60 kg/m³ in density. In an even more preferred embodiment the slabstock foam has a density of 40 kg/m³ or less.

A preferred slabstock foam formulation contains from 3 to 6, preferably 4 to 5 parts by weight water are used per 100 parts by weight high equivalent weight polyol at atmospheric
25 pressure. At reduced or increased pressure these levels are adjusted accordingly to obtain targeted densities, i.e., reduced pressure will generally decrease the density.

Polyurethane foams produced using polymeric polyol compositions of the invention can be used in applications known in the industry. For example, flexible, semi-flexible foams and find use in applications such as vehicle applications such as seats, sun visors, armrests, door
30 panels, noise and heat insulation parts, dashboards, or instrument panels. Exemplary placement of the foams includes locations such as under the carpet or in other parts of the car interior or in the engine compartment. Foam of the invention can also be used in many domestic applications such as shoe soles, cloth interliners, appliance, furniture, and bedding.

The polyurethane foams of the present invention may optionally be characterized by one
35 or more foam properties, including, but not limited to density, indentation force deflection

(IFD), sag factor, recovery ratio, guide factor, compression load deflection (CLD), percent compression set, tensile strength, elongation, aging tests, and tear strength.

Density is weight per unit volume (weight/volume) and typically expressed as lbs/ft³ (pcf) or g/L. Exemplary densities are in the range of about 20 g/L to about 80 g/L, or more
5 specifically in the range of about 25 g/L to about 32 g/L.

Compression force deflection (CFD), such as measured by the ISO 3386/1 standard, is a testing standard designed to measure the compression stress/strain (load divided by specimen surface area at a certain compression percentage) characteristic of foam. CFD is also a measure of firmness and is expressed in pounds per square inch (psi), at a given percentage deflection.
10 Exemplary densities are in the range of about 20 g/L to about 80 g/L, or more specifically in the range of about 25 g/L to about 32 g/L.

Percent compression set (CS), such as measured by the ISO 1856 standard, is a measure of the permanent deformation of a foam after it has been compressed between two metal plates for a controlled time period and temperature condition. The standard conditions are 22 hours at
15 70°C (158°F). Exemplary compression set values are in the range of about 1 to about 20, or more specifically in the range of about 5 to about 7.

Tensile properties is a measure according to ISO 1798 and tensile strength is the amount of force required to break an area of foam as it is pulled apart, and is generally expressed in pounds per square inch (psi). Foam compositions can be prepared to provide foam with a
20 desired tensile strength, or a tensile strength within a desired range.

Elongation, such as measured by the ISO 1798 standard, is a measure of the extent to which the foam can be stretched before it breaks and is expressed as a percentage of its original length. Elongation is measured at the same time, as tensile strength is determined; therefore, the sample size is the same. Exemplary elongation values are in the range of about 50 to about 200,
25 or more specifically in the range of about 110 to about 130.

Tear strength, such as measured by the ASTM D3574 standard, is a measure of the force required to continue a tear in foam after a split has been started and is expressed in pounds per linear inch (pli). Exemplary tear strengths are in the range of about 50 to about 350, or more specifically in the range of about 195 to about 230.

30 Emissions Measurements are done following VDA 278 (*Thermal Desorption Analysis of Organic Emissions for the Characterization of Non-Metallic Materials for Automobiles*) official protocol: - VOC value: volatile organic compounds (90°C, 30 min); Emission limits depend on car manufacturer, e.g., Daimler VOC ≤ 100 µg/g following VDA 278 testing protocol.

The following examples are given to illustrate the invention and should not be interpreted as limiting in anyway. Unless stated otherwise, all parts and percentages are given by weight.

EXPERIMENTAL

Preparation of Oligomeric Diaminopropane (DAPO).

1,3-diaminopropane (DAP, available from BASF Corp.) is reacted over a heterogeneous catalyst in a continuous packed bed reactor to form higher molecular weight oligomers of DAP. Examples of higher molecular weight oligomers include 1,7-diamino-4-azaheptane hereafter referred to as dipropylenetriamine (DPTA or Structure I where x is 0) and 1,11-diamino-4,8-diazaundecane hereafter referred to as tripropylenetetramine (TPTA or Structure I where x is 1). Structure I where x is 2 to 4 and higher is herein after referred to as higher molecular weight (Mw) oligomers.

The catalyst used is a Ni/Re 6.8/1.8 weight percent on an $\text{Al}_2\text{O}_3/\text{SiO}_2$, 80:20, 1/16 inch extrudate, surface area about 153 m^2/g . The reaction is run in a 1 inch (O.D.) by 8 foot packed bed reactor. The reactor bed is made of 1 inch seamless tubing (1 inch outside diameter, 0.095 in wall thickness). The length of the reactor tube filled with 400g catalyst is approximately 8 feet. The reactor tube is incased in a 1.5 inch diameter Swagelok tubing through which heat transfer fluid is pumped via a standard laboratory heating bath. This allows for nearly isothermal operation of the reactor tube. A multipoint thermocouple inside the tube reactor bed is used for temperature monitoring. Reaction pressure is monitored at the inlet and outlet of the reactor tube. The DAP (~99% pure) feed material is pumped via a 500 ml syringe pump through a flow meter and into the bottom of the reactor. Just prior to the reactor tube inlet (bottom), the hydrogen gas is introduced to the liquid DAP stream. Reaction pressure is varied from 200 to 1000 psig with a typical pressure ranging from 600 to 800 psig. At the reactor outlet, the pressure is let down to approximately 150 to 200 psi before sending the product mix to an intermediate tank. There is a sampling system that allows for a timed sample to be taken of the product stream. The sample time is dependent on the feed flow rate, but routinely samples are taken in the range of 15 to 30 minutes to collect 40 to 60 g liquid product sample. The sampling system consists of a stainless reservoir to collect DAP reaction mixture, followed by a small scrubber, and a wet test meter. This allows for quantification of the feed flow, ammonia generation, and hydrogen flow during sampling. The liquid product mixture (NH_3 and H_2 free) is analyzed by gas chromatography & liquid chromatography for quantification of the DAP oligomers. The reaction is run at various operating conditions to achieve selectivity to

higher DAP oligomers. **Error! Reference source not found.** includes four different operating conditions and the corresponding GC analysis of the product mix collected from the continuous reactor.

Table 1

Example	1	2	3	4
Temp (°C)	129	140	128.6	126.6
Pressure (psig)	746	800	190	812
DAP Flow (ml/min)	2.4	5	5	15
H ₂ Flow (SLPH)	9.8	9.6	9.6	10.2
Product wt%				
DAP	6.93	10.18	17.85	78.23
DPTA	16.6	18.93	32.88	19.88
TPTA	17.13	18.8	22.62	3.06
Higher Mw Oligomers	59.7	52.08	26.64	0
DAP Conversion (%)	93.06	89.8	82.11	21.62

The product mix from the reactor is further refined to remove un-reacted DAP. A distillation column (2 inch by 6 foot) is used for the refining of the 1,3-diaminopropane oligomers. 0.25" inch ceramic INTALOX™ saddles are used as column packing. The 11 liter reboiler still pot is heated by a heating bath that is capable of delivering 250°C. The system had a vacuum capability of 0.1 to 760 mmHg. The overheads are condensed by a double coil condenser capable of heating or cooling (-25 to 150°C). The distillation unit is equipped with a process control system for data collection and/or control. A typical distillation feed composition is shown in **Error! Reference source not found.**

High temperature ($\geq 250^{\circ}\text{C}$), low pressure (full vacuum to 10 mmHg) distillation conditions are required to remove the light boilers (1,3-DAP and x is 0 and higher) from the higher molecular weight amines.

Table 2

	Min wt%	Max wt%
DAP	12	29
DPTA	21	31
TPTA	18	20
Higher Oligomers	20	46

Error! Reference source not found. shows distillation results for a typical distillation batch with reboiler temperature up to 250°C and vacuum of about 1 mmHg (~ 10 mmHg pressure drops).

Table 3

	Min wt%	Max wt%
DAP	0.0	0.01
DPTA	0.04	0.05
TPTA	8.2	12.4
Higher Oligomers	88	92

Preparation of Partially Methylated Diaminopropane Oligomer (PMDAPO).

Oligomeric Diaminopropanes are characterized by electrospray ionization (ESI) in combination with liquid chromatography and mass spectroscopy (LC-MS). This is known as ESI/LC/MS and is a standard means of characterizing materials such as this and is well known to anyone skilled in this type of analytical procedure. LC-MS methodologies are mainly used for semi-volatile and non-volatile compounds and generally couple a gradient reversed-phase separation with MS detection using electrospray ionization (ESI) in both positive and negative ion modes.

Twenty five grams of water wet Raney Ni 5887-200 is transferred into a Robinson-Mahoney (RM) catalyst basket and quickly assembled into the 1 liter reactor. The reactor is pressurized and then vented three times to 500 psia with nitrogen and then another three times with hydrogen and drained any water out of the reactor with house nitrogen. The catalyst is

washed with 300g of n-butanol four times at 80°C and 1000 rpm. The catalyst is heated to 180°C under 500 psia of hydrogen pressure overnight prior to using in the methylation reaction.

225g of DAPO is pre-mixed with 125g of n-butanol. One hundred grams of n-butanol is used to flush the lines out prior to the addition of formaldehyde. Three hydrogen pressurization and venting cycles are completed prior to addition of formaldehyde. An operational objective is to maintain the temperature below 25°C during the addition of formaldehyde. Hydrogen flow is set to 100 sccm through the shot tube and the reactor set in pressure control mode at 15 psia. The 217g of 37 wt % formaldehyde in water is pumped through the 500 mL shot tube. The feed addition pump and transfer lines are flushed with 25g of n-butanol. An additional 75g of n-butanol is added to the process for a total of 325g of n-butanol after the formaldehyde is added. Time zero is established at the time the aldehyde addition commenced. The mixture is heated to 125°C at 750 psia hydrogen pressure and held for 24 hours. The temperature is then increased to 150°C and held for another 24 hours at which time no additional hydrogen uptake is observed. The mixture is distilled to 200°C and approximately 3 mmHg to remove water / n-butanol completely and yield the desired product (PMDAPO Example 5). The product is analyzed via standard NMR known in the art.

Preparation of a Polyol from PMDAPO.

Example 6. In a 5 liter stainless steel reactor, 148 g of Example 5 PMDAPO is charged and vacuum is applied. 87 g of propylene oxide is gradually fed inside the reactor at 140°C within 30 minutes. Reactor pressure is reaching 3 bar. After 2 hours of reaction of the free
5 propylene oxide, the pressure is coming back to vacuum (0 bar) and temperature is reduced to 120°C, before the addition of 12.7 g of a 45% water solution of KOH. The water is stripped out during 1 hour and 1218 g of propylene oxide are fed over a period of 6 hours at 3.5 bar. After 4
10 hours reaction, the temperature is increased to 135°C, before the addition of 534 g ethylene oxide during 2 hours at 2 bar. The digested product is treated with a magnesium silicate adsorbent to remove the KOH. The product characterizations are described in Table 4.

Table 4

Example 6	
Initiator Functionality	4.3
Initiator MW	427
Target MW	5160
Temperature autocatalytic (°C)	140
Temperature propoxylation with KOH (°C)	120
Temperature ethoxylation (°C)	135
KOH end batch (ppm)	2900
EO capping (%)	27
OH value (mg KOH/g)	71.6
Calculated MW	3369
Water (wt%)	0.043
Viscosity at 25°C (cSt)	1280
Potassium (ppm)	2.6
Sodium (ppm)	2.7
Basicity total (meq./g)	1.17

Preparation of Polyurethane Foam

A description of the raw materials used in the examples is as follows.

- 5 CP 1421 is a 1675 equivalent weight, trifunctional PO/EO polyol for cell opening available as VORANOL™ CP 1421 from The Dow Chemical Company;
- NC 632 is a 1,700 equivalent eight polyoxypropylene polyoxyethylene polyol initiated with a blend of glycerol and sorbitol available as SPECFLEX™ NC 632 from The Dow Chemical Company;
- 10 NC 138 is a 2040 equivalent weight, 15 % EO capped trifunctional PO/EO polyol available as VORANOL NC 138 from The Dow Chemical Company;
- DEOA is diethanol amine, available from Aldrich Chemical;
- NE 1070 is an amine gel catalyst non-emissive available as DABCO™ NE 1070 from Air Products;

- DMEE is (N,N-dimethylaminoethoxy) ethanol available as NIAX™ A-1 from Momentive Performance Materials;
- B 8715 LF2 Surfactant for foam stability available from Evonik;
- B 8736 LF2 Surfactant for foam stability available from Evonik;
- 5 NE 396 is a 30% NCO content MDI based isocyanate formulation available as SPECFLEX NE 396 from The Dow Chemical Company;
- NC 700 is a 49% solids content, having an OH number of 20 mg/g, copolymer polyol (CPP) for TDI and MDI formulations available as SPECFLEX NC 700 from The Dow Chemical Company
- 10 Glycerin is available from Aldrich Chemical;
- NE1090 is an amine gel catalyst non-emissive available as DABCO NE 1090 from Air Products;
- BA 305 is an additive product for improved humid aging available as DABCO BA 305 from Air Products;
- 15 NE 300 is a reactive non-emissive amine blowing catalysis available as DABCO NE 300 from Air Products;
- and
- T-80 is an 80:20 TDI mixture of 2,4 to 2,6 isomers available as VORANATE™ T-80 from The Dow Chemical Company.

20 The polyurethane foams are processed by dispensing the polyurethane reactive mixture by hand-mixing (Herrington & et.al., 1997). Fully formulated polyol and isocyanate components are conditioned separately at 25°C temperature for 30 min before foaming tests. The two components are mixed together in a metal cup at the required ratio reported in Table 5 and Table 6 using a mechanical overhead stirrer with a propeller blade at 1200 rpm speed for 12

25 sec.

The compositions for Comparative Example A and Examples 7 to 9 using MDI are given in Table 5, components are in parts per hundred (pph) unless otherwise noted. The liquid mixture is then immediately poured into a 0.5 liter paper cup, reactivity and growing profile has been measured by cream, gelling, and rise time and are reported in Table 5.

30 The compositions for Comparative Example B and Examples 10 to 12 using TDI are given in Table 6, components are in parts per hundred (pph) unless otherwise noted. The liquid mixture is then immediately poured into a 0.5 liter paper cup, reactivity and growing profile has been measured by cream, gelling, and rise time and are reported in Table 6.

35 The following physical properties for Comparative Examples A and B and Examples 7 to 12 are given in Tables 5 and 6:

Density is determined according to standard techniques of dividing foam weight by foam volume and reporting as lbs/ft² or Kg/m²;

CLD is compression load deflection at 40 % stress and is determined according to ISO 3386/1 before and after the following autoclave humid aging conditions: first day: sample in the steam autoclave (120°C to 100% RH) for 5 h, then 3 h in oven at 70°C, second day: sample in the steam autoclave (120°C to 100% RH) for 5 h, then 3 h in oven at 70°C, third day: sample in the steam autoclave (120°C- 100% RH) for 5 h, then 3 h in oven at 70°C, and then the test is performed 16h after the last cycle in oven, during those 16h the specimen is kept at 23°C and 50% RH;

and

Tear Strength is determined according to ASTM D3574 before and after autoclave humid aging as described above.

The compositions for Comparative Examples C and D and Examples 13 and 14 are given in Table 7, components are in weight percent unless otherwise noted. The liquid mixture is then immediately poured into a 0.5 liter paper cup. Volatile Emissions VOC and FOG Testing

per VDA 278 Testing Standard and the results are listed in Table 6. The VDA-278 (Verband der Automobilindustrie (VDA 278), 2011) guidelines are as follows:

20 General VDA-278 guidelines

All analyses are performed according to the standard method VDA-278 'Thermal Desorption Analysis of Organic Emissions for the Characterization of Non-Metallic Materials for Automobiles, updated October 2011. The VOC value according to VDA-278 is a measure for the total of readily volatile to medium volatile substances, and is calculated as the toluene equivalent of the total peak area of the GC-MS chromatogram up to n-pentacosane (C25 – in our case up to 49.4 min) obtained under VOC prescribed conditions (cf. below). The FOG value is the total of substances with low volatility, and is calculated as the hexadecane equivalent of the total GC-MS peak area of compounds eluting from the retention time of n-tetradecane (C14) up to n-dotriacontane (C32) (in our case 11.7 min up to 44.5 min) under FOG prescribed conditions. A separate table shows at least all substances with an emission value $\geq 1 \mu\text{g/g}$.

30 Sample preparation

The foam samples are conditioned at room temperature for 7 days (RH about 50 %). A piece of foam with skin was cut of about 1 cm length, with a width of a few mm, and weighing 15.0 mg \pm 2 mg. The exact weight is recorded with an analytical balance, and is mentioned in the tables. For each sample, two pieces of foam are cut and each was put in a thermal

desorption tube, which is closed immediately and analyzed as soon as possible. For the first tube, only the VOC measurement is performed, while for the second tube the FOG measurement is performed as well, immediately following the VOC analysis. The analytical parameters of the thermal desorption and GC-MS analysis, are gathered.

5 Calibration

Calibration is performed by means of a calibration solution of toluene in methanol (0.5 mg/ml) for the VOC analysis, and a hexadecane solution in methanol (0.5 mg/ml) for the FOG analysis. For this purpose, 4 µl of these solutions are loaded on a conditioned Tenax tube and analyzed. These standards are analyzed in triplicate to obtain representative average values.

- 10 All the results are quantified as toluene and hexadecane equivalents for the VOC and FOG analyses, respectively. A control solution consisting of 18 different compounds is analyzed regularly to check the performance of the system.

Table 5

	Comparative Example A	Example 7	Example 8	Example 9
A Side				
CP 1421	1.5	1.5	1.5	1.5
NC 632	30.2	30.2	30.2	30.2
NC 138	63.2	52.2	44.2	48.2
Example 7		12	20	16
Water	3.3	3.3	3.3	3.3
DEOA	0.35	0.35	0.35	0.35
NE 1070	0.9			
DMEE	0.1			
B 8715 LF2	0.45	0.45	0.45	0.45
Total pph	100	100	100	100
B Side				
NE 396 (MDI)	50	50	50	50
PROPERTIES				
Cream Time (s)	18	22	17	19
Gel Time (s)	95	139	79	115
Rise Time (s)	140	176	107	127
Density (g/L)	60	60	60	60
CLD 40% stress (K Pa)	10.6	14.4	13.7	15.5
CLD 40% stress after autoclave humid aging (KPa)	5.1	6.1	5.7	6.6
Compression Set	4.7	6.4	9.6	7.2
Tear Strength (N/m)	0.23	0.22	0.14	0.34
Tear Strength after autoclave humid aging (N/m)	0.19	0.29	0.21	0.26

Table 6

	Comparative Example B	Example 10	Example 11	Example 12
A Side				
CP 1421	38.97	27.55	19.55	23.55
NC 632	55	55	55	55
NC 138		12	20	16
Example 7	0.6	0.6	0.6	0.6
Water	0.5	0.5	0.5	0.5
DEOA	0.6	0.6	0.6	0.6
NE 1070	3.25	3.25	3.25	3.25
DMEE	0.3			
B 8715 LF2	0.5	0.5	0.5	0.5
VORANATE T-80	0.28			
Total pph	100	100	100	100
B Side				
NE 396 (MDI)	40	40	40	40
PROPERTIES				
Cream Time (s)	12	12	11	11
Gel Time (s)	63	87	57	74
Rise Time (s)	98	103	71	84
Density (g/L)	50	50	50	50
CLD 40% stress (K Pa)	14.8	19.7	19.5	20.1
CLD 40% stress after autoclave humid aging (KPa)	12.3	12.3	10.4	11.6
Compression Set	5.7	13.4	24.6	19.9
Tear Strength (N/m)	0.23	0.22	0.14	0.34
Tear Strength after autoclave humid aging (N/m)	0.19	0.29	0.21	0.26

Table 7

	Comparative Example C	Comparative Example D	Example 13	Example 14
A Side				
CP 1421	1.5		1.5	
NC 632	30.2	39.4	30.2	23.55
NC 138	63.2		48.2	
WATER	3.3	3.25	3.3	3.25
DEOA	0.35	0.6	0.35	0.6
B 8715 LF2	0.45		0.45	
DMEE	0.1			
DABCO NE 1070	0.9			
Example 7			16	16
NC 700		55		55
B 8736 LF2		0.6		0.6
Glycerin		0.5		0.5
DABCO BA 305				0.5
DABCO 33 LV		0.5		
DABCO A1		0.15		
TOTAL %	100	100	100	100
B Side				
Dow NE 396	50		50	
Voranate T-80		50		50

Table 8 shows the results for VOC emissions and FOG values for Comparative Examples C and D and Examples 13 and 14.

Table 8

	Amount (mg)	VOC Emission (µg/g)	FOG Value (µg/g)
Comparative Example C	16.7	88	-
Comparative Example C	16.9	82	391
Comparative Example D	13.3	235	-
Comparative Example D	15.8	225	148
Example 13	16.7	129	-
Example 13	12.7	119	122
Example 14	16.2	67	-
Example 14	12.8	62	143

- 5 Table 9 shows the breakdown of the compounds detected that make up the VOC emission of the foam samples, grouped according to chemical functionality, expressed as toluene equivalent in µg /g.

Table 9

10

	Comp. Ex. C		Comp. Ex. D		Example 13		Example 14	
COMPOUNDS	%	µg/g	%	µg/g	%	µg/g	%	µg/g
glycol ether isomers	1.2	1.1	0.9	2.2	11.0	14.1	2.5	1.7
siloxanes	66.8	58.6	13.5	31.8	64.6	83.2	42.9	28.9
amine catalysts	1.7	1.5	68.1	160.3	ND	ND	ND	ND
alkyl diphenylamines	1.6	1.4	0.7	1.8	1.1	1.4	2.5	1.7
CPP compounds	2.1	1.9	9.9	23.3	ND	ND	31.2	21.1
unknown/other	9.8	8.6	1.1	2.6	9.0	11.6	2.2	1.5

Table 10 shows the breakdown of the compounds detected that make up the FOG value of the foam samples, grouped according to chemical functionality, expressed in hexadecane equivalent in µg/g.

Table 10

	Comp. Ex. C		Comp. Ex. D		Example 13		Example 14	
COMPOUNDS	%	µg/g	%	µg/g	%	µg/g	%	µg/g
glycol ether isomers	1.3	5.1	0.9	1.1	12.2	19.4	ND	ND
amine catalysts	58.8	227.0	ND	ND	0.6	1.0	ND	ND
alkyl diphenylamines	16.8	64.9	43.6	54.4	38.5	61.3	34.1	53.8
CPP compounds	ND	ND	9.4	11.7	ND	ND	7.8	12.4
unknown/other	18.3	70.6	33.9	42.3	40.8	65.0	47.7	75.3

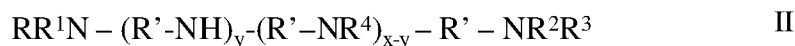
It is clearly shown that the inventive Examples 13 and 14 have low to non-detectable

5 levels of amines releasing from the foam per the VDA 278 test protocol compared to the emissive amine catalysts of the Comparative Examples C and D. The Comparative Example C shows that the non-emissive amine catalyst such as Air Products NE 1070 used in MDI PU foams has low amine emissions in the VOC test it shows 200 times more amine release in the FOG test than Example. The standard TEDA with NIAX A1 catalyst combination used

10 commonly in the industry for TDI foams is shown in Comparative Example D compared to inventive Example 14. The data in the VOC test at 160 times greater for the Comparative Example D than the inventive Example 14 showing non-detectable levels of amine for both the VOC and FOG parts of the VDA 278 test protocol.

What is claimed is:

1. A polymeric amine composition comprising one or more amine compound represented by the Structure II:



wherein R' is a branched or linear C₁ to C₆ alkyl group,

R, R¹, R², and R³ are independently a hydrogen or a C₁ to C₆ linear or branched alkyl group with the proviso that at least one of R, R¹, R², and R³ is not hydrogen,

R⁴ is a hydrogen or a C₁ to C₆ linear or branched alkyl group,

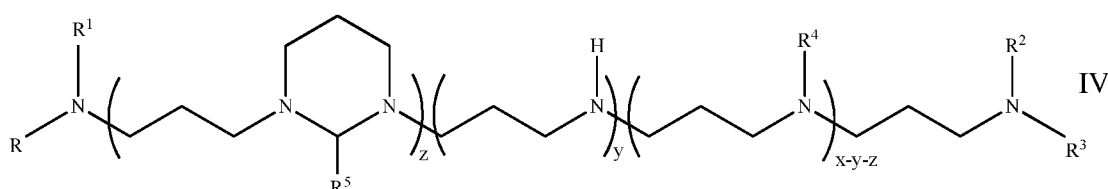
x is from 1 to 33,

and

y is from 0 to 32,

with the proviso that that x-y is equal to or greater than 1 and the number of N-H bonds in (II) is greater than 0 and less than 8.

2. The polymeric amine composition of Claim 1 wherein R' is a C₃ alkyl group and the one or more amine compound represented by the Structure IV:



wherein R, R¹, R², and R³ are independently a hydrogen or a C₁ to C₆ linear or branched alkyl group with the proviso that at least one of R, R¹, R², and R³ is not hydrogen,

R⁴ is a hydrogen or a C₁ to C₆ linear or branched alkyl group,

R⁵ is a hydrogen or a C₁ to C₅ linear or branched alkyl group,

x is from 1 to 33,

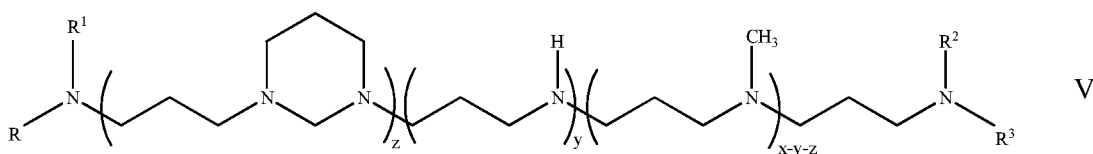
y is from 0 to 32,

and

z is from 0 to 15,

with the proviso that that x-y-z is equal to or greater than 2 and the number of N-H bonds in (IV) is greater than 0 and less than 8.

3. The polymeric amine composition of Claim 1 wherein the one or more amine compound is represented by the Structure V:



wherein R, R¹, R², and R³ are independently a hydrogen or a methyl group with the proviso that at least one of R, R¹, R², and R³ is not hydrogen,

x is from 1 to 33,

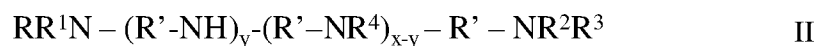
y is from 0 to 32,

and

z is from 0 to 15,

with the proviso that that x-y-z is equal to or greater than 2 and the number of N-H bonds in (V) is greater than 0 and less than 8.

4. A polymeric polyol composition comprising the reaction product(s) of:
 - (i) a polymeric amine composition comprising one or more amine compound represented by the Structure II:



wherein R' is a branched or linear C₁ to C₆ alkyl group,

R, R¹, R², and R³ are independently a hydrogen or a C₁ to C₆ linear or branched alkyl group with the proviso that at least one of R, R¹, R², and R³ is not hydrogen,

R⁴ is a hydrogen or a C₁ to C₆ linear or branched alkyl group,

x is from 1 to 33,

and

y is from 0 to 32,

with the proviso that that x-y is equal to or greater than 1 and the number of N-H bonds in (II) is greater than 0 and less than 8.

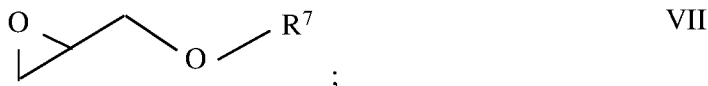
and

- (ii) at least one epoxide compound having the structure IV:



or

at least one glycidyl ether compound having the structure VII:



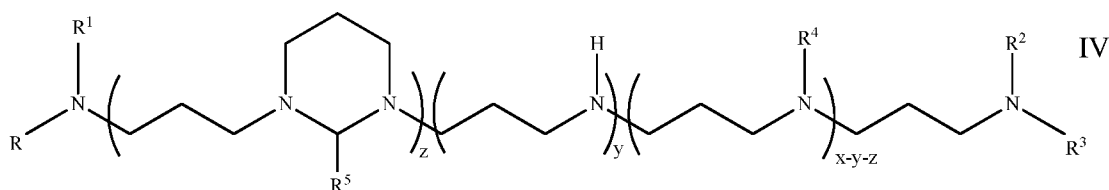
or a combination thereof;

wherein R^6 is hydrogen, phenyl, cyclohexyl, or a C_1 to C_{18} linear or branched alkyl

and

R^7 is hydrogen, phenyl, a C_1 to C_6 linear or branched alkyl-substituted phenyl, or a C_1 – C_{18} linear or branched alkyl.

5. The polymeric polyol composition of Claim 4 wherein the one or more amine compound is represented by the Structure IV:



wherein R , R^1 , R^2 , and R^3 are independently a hydrogen or a C_1 to C_6 linear or branched alkyl group with the proviso that at least one of R , R^1 , R^2 , and R^3 is not hydrogen,

R^4 is a hydrogen or a C_1 to C_6 linear or branched alkyl group,

R^5 is a hydrogen or a C_1 to C_5 linear or branched alkyl group

x is from 1 to 33,

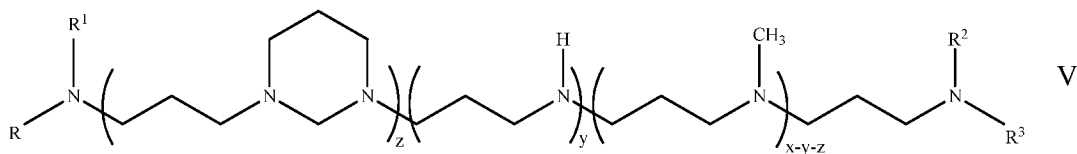
y is from 0 to 32,

and

z is from 0 to 15,

with the proviso that that $x-y-z$ is equal to or greater than 2 and the number of N-H bonds in (IV) is greater than 0 and less than 8.

6. The polymeric polyol of Claim 4 wherein the one or more amine compound is represented by the Structure V:



wherein R, R¹, R², and R³ are independently a hydrogen or a methyl group with the proviso that at least one of R, R¹, R², and R³ is not hydrogen,

x is from 1 to 33,

y is from 0 to 32,

and

z is from 0 to 15,

with the proviso that that x-y-z is equal to or greater than 2 and the number of N-H bonds in (V) is greater than 0 and less than 8.

7. A process to make a polyurethane polymer by reaction of a mixture comprising:
 - (A) a polymeric polyol formulation comprising the polymeric polyol composition of Claim 4;
 - (B) at least one organic isocyanate;
 - (C) optionally a blowing agent;and
 - (D) optionally additives or auxiliary agents known per se for the production of polyurethane polymers.
8. The process of Claim 7 wherein the reaction occurs in the presence of a blowing agent and the polyurethane polymer is produced in the form of a polyurethane flexible foam.
9. A process to make a polyurethane polymer by reaction of a mixture comprising:
 - (A) a polymeric polyol formulation comprising the polymeric polyol composition of Claim 5;
 - (B) at least one organic isocyanate;
 - (C) optionally a blowing agent;and
 - (D) optionally additives or auxiliary agents known per se for the production of polyurethane polymers.
10. The process of Claim 9 wherein the reaction occurs in the presence of a blowing agent and the polyurethane polymer is produced in the form of a polyurethane flexible foam.
11. A process to make a polyurethane polymer by reaction of a mixture comprising:
 - (A) a polymeric polyol formulation comprising the polymeric polyol composition of Claim 6;
 - (B) at least one organic isocyanate;
 - (C) optionally a blowing agent;and

(D) optionally additives or auxiliary agents known per se for the production of polyurethane polymers.

12. The process of Claim 11 wherein the reaction occurs in the presence of a blowing agent and the polyurethane polymer is produced in the form of a polyurethane flexible foam.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2016/035642

A. CLASSIFICATION OF SUBJECT MATTER INV. C08G18/48 C08G18/50 C08G18/63 C08G18/66 C08G18/76 C08G18/32 C08G73/02 ADD. 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) 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 practicable, search terms used) EPO-Internal, WPI Data																	
C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%;">Category*</th> <th style="width: 70%;">Citation of document, with indication, where appropriate, of the relevant passages</th> <th style="width: 20%;">Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td>US 2009/227695 A1 (BURDENIUC JUAN JESUS [US] ET AL) 10 September 2009 (2009-09-10) cited in the application paragraphs [0003] - [0005] paragraphs [0190], [0198] -----</td> <td style="text-align: center; vertical-align: top;">1-12</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td>US 2010/240783 A1 (BURDENIUC JUAN JESUS [US] ET AL) 23 September 2010 (2010-09-23) paragraphs [0004], [0005] example 1 -----</td> <td style="text-align: center; vertical-align: top;">4-12</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td>WO 95/09832 A1 (MERRELL DOW PHARMA [US]) 13 April 1995 (1995-04-13) pages 7-10 page 9, line 32 -----</td> <td style="text-align: center; vertical-align: top;">1-3</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td>US 5 885 955 A (UNO MITSURU [JP] ET AL) 23 March 1999 (1999-03-23) column 8, line 60 -----</td> <td style="text-align: center; vertical-align: top;">1-3</td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	X	US 2009/227695 A1 (BURDENIUC JUAN JESUS [US] ET AL) 10 September 2009 (2009-09-10) cited in the application paragraphs [0003] - [0005] paragraphs [0190], [0198] -----	1-12	X	US 2010/240783 A1 (BURDENIUC JUAN JESUS [US] ET AL) 23 September 2010 (2010-09-23) paragraphs [0004], [0005] example 1 -----	4-12	X	WO 95/09832 A1 (MERRELL DOW PHARMA [US]) 13 April 1995 (1995-04-13) pages 7-10 page 9, line 32 -----	1-3	X	US 5 885 955 A (UNO MITSURU [JP] ET AL) 23 March 1999 (1999-03-23) column 8, line 60 -----	1-3
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X	US 2009/227695 A1 (BURDENIUC JUAN JESUS [US] ET AL) 10 September 2009 (2009-09-10) cited in the application paragraphs [0003] - [0005] paragraphs [0190], [0198] -----	1-12															
X	US 2010/240783 A1 (BURDENIUC JUAN JESUS [US] ET AL) 23 September 2010 (2010-09-23) paragraphs [0004], [0005] example 1 -----	4-12															
X	WO 95/09832 A1 (MERRELL DOW PHARMA [US]) 13 April 1995 (1995-04-13) pages 7-10 page 9, line 32 -----	1-3															
X	US 5 885 955 A (UNO MITSURU [JP] ET AL) 23 March 1999 (1999-03-23) column 8, line 60 -----	1-3															
<div style="display: flex; justify-content: space-between;"> <div> <input type="checkbox"/> Further documents are listed in the continuation of Box C. </div> <div> <input checked="" type="checkbox"/> See patent family annex. </div> </div>																	
<div style="display: flex;"> <div style="flex: 1;"> <p>* Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="flex: 1;"> <p>"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</p> <p>"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</p> <p>"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</p> <p>"&" document member of the same patent family</p> </div> </div>																	
Date of the actual completion of the international search <div style="text-align: center; font-size: 1.2em;">9 August 2016</div>		Date of mailing of the international search report <div style="text-align: center; font-size: 1.2em;">17/08/2016</div>															
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer <div style="text-align: center; font-size: 1.2em;">Bergmeier, Martin</div>															

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2016/035642

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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			US 5885955 A 23-03-1999
