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(54) Title: METAL SALTS OF AMINIO ACID TRIAZINES AS POLYURETHANE AND POLYISOCYANURATE CATALYSTS

(57) Abstract: The present disclosure provides a catalyst comprising a reaction product of (i) an aldehyde; and (ii) a metal salt of an aminocarboxylic acid. The catalyst may be used in the preparation of polyurethane or polyisocyanurate foam.

METAL SALTS OF AMINO ACID TRIAZINES AS POLYURETHANE AND POLYISOCYANURATE CATALYSTS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to United States Provisional Serial No. 62/309,567 filed March 17, 2016. The noted application is incorporated herein by reference.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0002] Not applicable.

FIELD OF THE INVENTION

[0003] The present disclosure provides a catalyst comprising a reaction product of an aldehyde and a metal salt of an aminocarboxylic acid. The catalyst according to the present disclosure is easily manufactured, exhibits high catalytic activity, good stability and is especially suitable for use in the preparation of polyurethane and polyisocyanurate foam.

BACKGROUND

[0004] Typically, polyisocyanurate and polyurethane foams are made by reacting a polyol and a polyisocyanate in the presence of a catalyst. Additional additives, such as blowing agents, surfactants and flame retardants, can also be present. The reactions for forming the polyurethane or polyisocyanurate foam consist mainly of a urethane bond-forming reaction (gelling reaction) by the reaction of the polyol with the polyisocyanate, a urea group-forming reaction (blowing reaction) by the reaction of the polyisocyanate with water, and an

isocyanurate ring-forming reaction (trimerization reaction) by trimerization of the polyisocyanate.

[0005] Known catalysts for accelerating the gelling reaction and/or blowing reaction include tertiary amine catalysts and organic metal catalysts. Among such tertiary amine catalysts, those industrially used may, for example, be compounds such as triethylenediamine, N,N,N',N'-tetramethyl-1,6-hexanediamine, N,N-dimethylcyclohexylamine, bis(2-dimethylaminoethyl) ether, N,N,N',N",N"-pentamethyldiethylenetriamine, N-methylmorpholine and N-ethylmorpholine. Organic metal catalysts generally include organolead, organoferric and organotin compounds, such as stannous chloride, and tin salts of carboxylic acids.

[0006] Also effective as catalysts are Mannich condensation products formed from nonylphenol, formaldehyde and a primary or secondary amine. However, in recent years, nonylphenol and related chemical forms of nonylphenol have raised concerns because of their effects on the endocrine system. Such concerns have led to many regulations and restrictions on the use of nonylphenol throughout the world.

[0007] Finally, triazines of a primary amine containing tertiary amines are known catalysts for polyurethane and to a lesser degree polyisocyanurate foams. One such catalyst is tris-dimethylaminopropyl-S-triazine which is the reaction product of dimethylaminopropylamine and formaldehyde. However, this catalyst has been bound to be unstable and decomposes at 120°C causing its activity to decrease during the foaming reaction as the foam internal temperature rises.

[0008] Thus, there exists a need to develop new catalysts which have the same or higher catalytic activity than state of the art catalysts based on nonylphenol and will also not decompose at high temperatures.

SUMMARY

[0009] In one aspect, there is provided a catalyst substantially free of nonylphenol which is suitable for use in the preparation of a polyurethane or polyisocyanurate foam. The catalyst according to the present disclosure includes a reaction product of: (i) an aldehyde; and (ii) a metal salt of an aminocarboxylic acid.

[0010] In a second aspect, there is provided a polyurethane or polyisocyanurate foam composition that contains the catalyst according to the present disclosure.

[0011] In a third aspect, there is provided a process for preparing a polyurethane or polyisocyanurate foam utilizing the catalyst according to the present disclosure.

[0012] In a fourth aspect, there is provided a polyurethane or polyisocyanurate foam obtained by bringing together, under foam-forming conditions, a polyisocyanate, a polyol, a blowing agent and the catalyst according to the present disclosure.

DETAILED DESCRIPTION

[0013] If appearing herein, the term "comprising" and derivatives thereof are not intended to exclude the presence of any additional component, step or procedure, whether or not the same is disclosed herein. In order to avoid any doubt, all compositions claimed herein through use of the term "comprising" may include any additional additive, adjuvant, or compound, unless stated to the contrary. In contrast, the term, "consisting essentially of" if appearing herein, excludes from the scope of any succeeding recitation any other component, step or procedure, except those that are not essential to operability and the term "consisting of", if used, excludes any component, step or procedure not

specifically delineated or listed. The term "or", unless stated otherwise, refers to the listed members individually as well as in any combination.

[0014] The articles "a" and "an" are used herein to refer to one or to more than one (i.e. to at least one) of the grammatical objects of the article. By way of example, "an amine" means one amine or more than one amine. The phrases "in one embodiment", "according to one embodiment" and the like generally mean the particular feature, structure, or characteristic following the phrase is included in at least one embodiment of the present disclosure, and may be included in more than one embodiment of the present disclosure. Importantly, such phrases do not necessarily refer to the same embodiment. If the specification states a component or feature "may", "can", "could", or "might" be included or have a characteristic, that particular component or feature is not required to be included or have the characteristic.

[0015] The term "substantially free" means, when used with reference to the substantial absence of a material, that such a material is present, if at all, as an incidental impurity or by-product. For instance in some embodiments, the material may be present in the composition of matter at an amount of no more than 100 ppm, in some instances less than 20 ppm and in still other instances less than 1 ppm.

[0016] According to one aspect, the present disclosure provides a catalyst comprising a reaction product of: (i) an aldehyde; and (ii) a metal salt of an aminocarboxylic acid. The catalyst according to the present disclosure exhibits surprisingly high catalytic activity, good stability (i.e. does not decompose at high temperatures like state of the art triazine catalysts) and is easy to manufacture. Moreover, the catalyst is substantially free of nonylphenol, making it environmentally safe to use in countries and specific regions that have banned the use of nonylphenol.

[0017] According to one aspect, the aldehyde which may be used in the preparation of the catalyst according to the present disclosure is an aliphatic aldehyde and/or an aromatic aldehyde. The aliphatic aldehyde may be a C_1 to C_6 aldehyde, such as formaldehyde, acetaldehyde, propionaldehyde, butyraldehyde, valeraldehyde, and hexanal aldehyde. The aromatic aldehyde may be benzaldehyde and salicylaldehyde. In other aspects, a heterocyclic aldehyde for use herein is furfural and thiophene aldehyde, etc. Also useful are formaldehyde-producing reagents such as paraformaldehyde, or aqueous formaldehyde solutions such as formalin. In one particular embodiment, the aldehyde is formaldehyde or formalin.

[0018] According to another aspect, the aminocarboxylic acid is selected from an α-amino acid, a β-amino acid, a γ-amino acid, a δ-amino acid, a ε-amino acid and a ζ-amino acid.

[0019] Examples of α-amino acids include glycine (aminoacetic acid), N-methylglycine (N-methylaminoacetic acid, sarcosine), N-ethylglycine, alanine (2-aminopropionic acid), N-methylalanine (2-(methylamino)propionic acid), N,N-dimethylalanine, N-ethylalanine, 2-methylalanine (2-aminoisobutyric acid), leucine (2-amino-4-methylpentan-1-oic acid), N-methylleucine, N,N-dimethylleucine, isoleucine (1-amino-2-methylpentanoic acid), N-methylisoleucine, valine (2-aminoisovaleric acid), α-methylvaline (2-amino-2-methylisovaleric acid), N-methylvaline (2-methylaminoisovaleric acid), proline (pyrrolidine-2-carboxylic acid), N-methylproline, serine (2-amino-3-hydroxypropan-1-oic acid), N-methylserine, 2-(methylamino)isobutyric acid, piperidine-2-carboxylic acid and N-methylpiperidine-2-carboxylic acid.

[0020] Examples of β-amino acids include 3-aminopropionic acid (β-alanine), 3-methylaminopropionic acid, iminodipropionic acid, N-methyliminodipropionic acid, piperidine-3-carboxylic acid and N-methylpiperidine-3-carboxylic acid.

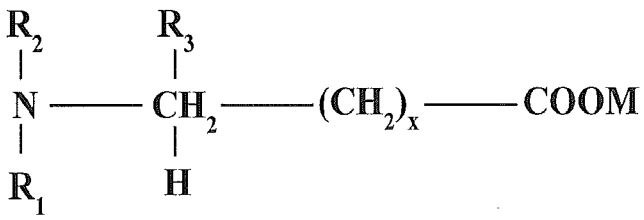
[0021] Examples of γ-amino acids include 4-aminobutyric acid and 4-methylaminobutyric acid.

[0022] Other aminocarboxylic acids include piperidine-4-carboxylic acid and N-methylpiperidine-4-carboxylic acid.

[0023] In one particular embodiment suitable aminocarboxylic acids include N-mono-C_1-C_4-alkylaminocarboxylic acids, in particular N-mono-C_1-C_4-alkyl-α-aminocarboxylic acids.

[0024] The metal salt is generally an alkali metal or alkaline earth metal salt. In one particular embodiment, the metal salt is an alkali metal salt such as a sodium, lithium, rubidium, cesium, francium or potassium salt, or an alkaline earth metal salt such as a magnesium, beryllium, barium or calcium salt.

[0025] According to one particular embodiment, the metal salt of the aminocarboxylic acid is a compound of the formula



where R_1, R_2, and R_3 are, independently of one another, H or a C_1-C_3 alkyl group, M is sodium or potassium and x is an integer from 0 to 5.

[0026] In another particular embodiment, the metal salt of the aminocarboxylic acid is the sodium salt of N-methylglycine or the potassium salt of N-methylglycine. In another particular embodiment, the metal salt of the

aminocarboxylic acid is the sodium salt of glycine or the potassium salt of glycine.

[0027] The catalyst can be prepared by reacting the aldehyde with the metal salt of an aminocarboxylic acid. In one embodiment, the reaction occurs by contacting the aldehyde and the metal salt of an aminocarboxylic acid in a reaction zone. The reactants may be contacted for a time and under conditions effective to react the aldehyde and reactive amine groups of the metal salt of the aminocarboxylic acid to form the catalyst.

[0028] The conditions of temperature and pressure under which the reaction occurs can vary widely, and generally temperatures from about 0°C to 80°C can be used. The pressures in the reaction zone will be sufficient to maintain a liquid reaction medium, and generally pressures from about 0.1 kPa to 1000 kPa, such as from about 1 kPa to 100 kPa, can be employed.

[0029] The reaction can be carried out in a batchwise, continuous or semicontinuous manner, in one or more reaction zones. The reaction can be conducted in any conventional apparatus such as stirred tank reactors, tubular flow reactors and the like.

[0030] The reactants can be charged to the reaction zone continuously or intermittently, together or sequentially, in any order. Generally, the metal salt of the aminocarboxylic acid, and any carrier or solvent for the reaction, will first be charged to the reaction zone, followed by the aldehyde reactant.

[0031] The reaction can be accomplished using a wide range of ratios of reactants, and the metal salt of an aminocarboxylic acid:aldehyde may be generally charged in a ratio of from 1:0.01 to 1:50, and in some embodiments from 1:0.2: to 1:10 , and in still more embodiments from 1:0.5 to 1:5, molar equivalents of metal salt of an aminocarboxylic acid:moles of aldehyde.

[0032] The reaction can be conducted in bulk (no diluent or solvent) or in a diluent or solvent. In one particular embodiment, the reaction is conducted in a solvent. Examples of diluents and solvents include water, ethylene glycol, propylene glycol, diethylene glycol, dipropylene glycol, as well as polyethylene or polypropylene glycols in the 100-1000 molecular weight range, benzene, toluene and xylene. Water that is evolved during the reaction can be removed by azeotropic distillation during the course of the reaction or after the completion of the reaction. For instance in one embodiment, the temperature and pressure can be maintained at about 80°C and about 40 mm Hg reduced pressure after completion of the reaction to remove water that has evolved. Typical reaction times may range from about 0.5 to about 12 hours, although longer or shorter times can be used as necessary or as desired.

[0033] According to another aspect of the present disclosure, there is provided a polyurethane or polyisocyanurate foam composition containing an isocyanate, a polyol, a blowing agent and the catalyst according to the present disclosure. The polyurethane or polyisocyanurate foam compositions according to the present disclosure are usually divided up into two components. The isocyanate portion is generally referred to as the A-side and the polyol portion is referred to as the B-side. Thus, in embodiments where the polyurethane or polyisocyanurate foam composition includes an A-side containing an isocyanate and a B-side containing a polyol, each of the remaining components of the foam composition may be included in either the A-side or B-side or they can be included as a separate component(s).

[0034] The isocyanate in the foam composition may be selected from a wide variety of isocyanates, including those that are well known to one skilled in the art. For example, organic polyisocyanates, modified multi-functional polyisocyanates, isocyanate-based prepolymers, and mixtures thereof may be employed. These may further include aliphatic and cycloaliphatic isocyanates, and in particular aromatic and, more particularly, multifunctional aromatic

isocyanates. Polyphenyl polymethylene polyisocyanates (PMDI) may also be used.

[0035] In one embodiment, the isocyanate includes 2,4- and 2,6-toluenediisocyanate and the corresponding isomeric mixtures; 4,4'-, 2,4'- and 2,2'-diphenyl-methanediisocyanate and the corresponding isomeric mixtures; mixtures of 4,4'-, 2,4'- and 2,2'-diphenyl-methanediisocyanates and polyphenyl polymethylene polyisocyanates (PMDI); and mixtures of PMDI and toluene diisocyanates. Also useful herein are aliphatic and cycloaliphatic isocyanate compounds, such as 1,6-hexamethylenediisocyanate; 1-isocyanato-3,5,5-trimethyl-1,3-isocyaantomethylcyclohexane; 2,4- and 2,6-hexahydrotoluene-diisocyanate and their corresponding isomeric mixtures; and 4,4'-, 2,2'- and 2,4'-dicyclohexyl-methanediisocyanate and their corresponding isomeric mixtures. Also useful is 1,3-tetra-methylene xylene diisocyanate.

[0036] In another embodiment, the isocyanate is a so-called modified multifunctional polyisocyanate, that is, a product which is obtained through chemical reaction of the above diisocyanates and/or polyisocyanates. Examples include polyisocyanates containing esters, ureas, biurets, allophanates and, preferably, carbodiimides and/or uretonomine, and isocyanurate and/or urethane group-containing diisocyanates or polyisocyanates. Liquid polyisocyanates containing carbodiimide groups, uretonomine groups and/or isocyanurate rings, having isocyanate group (NCO) contents of from 120 to 40 weight percent, or from 20 to 35 weight percent, can also be used. These include, for example, polyisocyanates based on 4,4'-2,4'- and/or 2,2'-diphenylmethane diisocyanate and the corresponding isomeric mixtures, 2,4- and/or 2,6-toluenediisocyanate and the corresponding isomeric mixtures; mixtures of diphenylmethane diisocyanates and PMDI; and mixtures of toluenediisocyanates and PMDI and/or diphenylmethane diisocyanates.

[0037] Suitable isocyanate-based prepolymers are prepolymers having NCO contents of from 2 to 40 weight percent, or from 4 to 30 weight percent. These prepolymers are prepared by reaction of the di- and/or polyisocyanates with materials including lower molecular weight diols and triols, but also can be prepared with multivalent active hydrogen compounds such as di- and tri-amines and di- and tri-thiols. Individual examples include aromatic polyisocyanates containing urethane groups, which may have NCO contents of from 5 to 40 weight percent, or 20 to 35 weight percent, obtained by reaction of diisocyanates and/or polyisocyanates with, for example, polyols such as lower molecular weight diols, triols, oxyalkylene glycols, dioxyalkylene glycols, or polyoxyalkylene glycols having molecular weights up to about 800. These polyols can be employed individually or in mixtures as di- and/or polyoxyalkylene glycols. For example, diethylene glycols, dipropylene glycols, polyoxyethylene glycols, ethylene glycols, propylene glycols, butylene glycols, polyoxypropylene glycols and polyoxypropylene polyoxyethylene glycols can be used. Polyester polyols can also be used, as well as alkyl diols such as butane diol. Other diols also useful include bishydroxyethyl- or bishydroxypropyl-bisphenol A, cyclohexane dimethanol, and bishydroxyethyl hydroquinone.

[0038] The isocyanate may be used in an amount sufficient to provide an isocyanate index of at least 80. Isocyanate index is calculated as the number of reactive isocyanate groups provided by the isocyanate divided by the number of isocyanate-reactive groups in the polyurethane or polyisocyanurate foam composition (including those contained by blowing agents such as water) and multiplying by 100. Water is considered to have two isocyanate-reactive groups per molecule for purposes of calculating isocyanate index. In one embodiment, the isocyanate index is from about 80 to about 600. For polyurethane foam applications, the isocyanate index may generally be from about 80 to 150. For polyisocyanurate foam applications, the isocyanate index may generally be greater than about 150 and up to about 600.

[0039] Polyols which may be present in the foam composition include one or more polyester or polyether polyols of the kind typically employed in processes to make polyurethane or polyisocyanurate foam. Other compounds having at least two isocyanate reactive hydrogen atoms may also be present, for example: polythioether polyols; condensate adducts of phenol and formaldehyde with one or more alkylene oxides including ethylene oxide, propylene oxide, and butylene oxide; polyester amides and polyacetals containing hydroxyl groups; aliphatic polycarbonates containing hydroxyl groups; amine terminated polyoxyalkylene polyethers; and graft dispersion polyols. Mixtures of two or more of the aforesaid materials may also be employed.

[0040] The term "polyester polyol" as used herein includes any minor amounts of unreacted polyol remaining after the preparation of the polyester polyol and/or unesterified polyol (for example, glycol) added after the preparation of the polyester polyol. Polyester polyols can be produced, for example, from organic dicarboxylic acids with 2 to 12 carbons, including aliphatic dicarboxylic acids with 4 to 6 carbons, and divalent and multivalent alcohols, including diols, with 2 to 12 carbons, such as, 2 to 6 carbons. Examples of dicarboxylic acids include succinic acid, glutaric acid, adipic acid, suberic acid, azelaic acid, sebacic acid, decanedicarboxylic acid, maleic acid, fumaric acid, phthalic acid, isophthalic acid, and terephthalic acid. The dicarboxylic acids can be used individually or in mixtures. Instead of the free dicarboxylic acids, the corresponding dicarboxylic acid derivatives may also be used, such as dicarboxylic acid mono- or di-esters of alcohols with 1 to 4 carbons, or dicarboxylic acid anhydrides. Dicarboxylic acid mixtures of succinic acid, glutaric acid and adipic acid in quantity ratios of 20-35:35-50:20-32 parts by weight may also be used. Examples of divalent and multivalent alcohols include ethanediol, diethylene glycol, 1,2- and 1,3-propanediol, dipropylene glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,10-decanediol, glycerine and trimethylolpropanes, tripropylene glycol, tetraethylene glycol, tetrapropylene glycol, tetramethylene glycol, 1,4-

cyclohexane-dimethanol, ethanediol, diethylene glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, or mixtures of at least two of these diols, especially mixtures of 1,4-butanediol, 1,5-pentanediol, and 1,6-hexanediol. Furthermore, polyester polyols of lactones, for example, ε-caprolactone or hydroxycarboxylic acids, for example, ω-hydroxycaproic acid, may also be used.

[0041] Polyether polyols that may be used include those which can be obtained by known methods, For example, polyether polyols can be produced by anionic polymerization with alkali hydroxides such as sodium hydroxide or potassium hydroxide or alkali alcoholates, such as sodium methylate, sodium ethylate, or potassium ethylate or potassium isopropylate as catalysts and with the addition of at least one initiator molecule containing 2 to 8, such as 3 to 8, reactive hydrogens or by cationic polymerization with Lewis acids such as antimony pentachloride, boron trifluoride etherate, etc., or bleaching earth as catalysts from one or more alkylene oxides with 2 to 4 carbons in the alkylene radical. Any suitable alkylene oxide may be used such as 1,3-propylene oxide, 1,2- and 2,3-butylene oxide, amylene oxides, styrene oxide, and preferably ethylene oxide and 1,2-propylene oxide and mixtures of these oxides. The polyalkylene polyether polyols may be prepared from other starting materials such as tetrahydrofuran and alkylene oxide-tetrahydrofuran mixtures; epihalohydrins such as epichlorohydrin; as well as aralkylene oxides such as styrene oxide. The polyalkylene polyether polyols may have either primary or secondary hydroxyl groups, preferably secondary hydroxyl groups from the addition of propylene oxide onto an initiator because these groups are slower to react. Included among the polyether polyols are polyoxyethylene glycol, polyoxypropylene glycol, polyoxybutylene glycol, polytetramethylene glycol, block copolymers, for example, combinations of polyoxypropylene and polyoxyethylene glycols, poly-1,2-oxybutylene and polyoxyethylene glycols, poly-1,4-tetramethylene and polyoxyethylene glycols, and copolymer glycols prepared from blends or sequential addition of two or more alkylene oxides. The

polyalkylene polyether polyols may be prepared by any known process such as, for example, the process disclosed by Wurtz in 1859 and Encyclopedia of Chemical Technology, Vol. 7, pp. 257-262, published by Interscience Publishers, Inc. (1951) or in U.S. Pat. No. 1,922,459.

[0042] In one particular embodiment, the polyether polyol includes the alkylene oxide addition products of polyhydric alcohols such as ethylene glycol, propylene glycol, dipropylene glycol, trimethylene glycol, 1,2- butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,7-heptanediol, hydroquinone, resorcinol glycerol, glycerine, 1,1,1-trimethylol-propane, 1,1,1-trimethylolethane, pentaerythritol, 1,2,6-hexanetriol, a-methyl glucoside, sucrose, and sorbitol. Also included within the term "polyhydric alcohol" are compounds derived from phenol such as 2,2-bis(4-hydroxyphenyl)-propane, commonly known as Bisphenol A. Also included may be a polyol which is initiated with a compound having at least two primary or secondary amine groups, a polyhydric alcohol having 4 or more hydroxyl groups, such as sucrose, or a mixture of initiators employing a polyhydric alcohol having at least 4 hydroxyl groups and compounds having at least two primary or secondary amine groups. Suitable organic amine initiators which may be condensed with alkylene oxides include aromatic amines-such as aniline, N-alkylphenylene-diamines, 2,4'-, 2,2'-, and 4,4'-methylenedianiline, 2,6- or 2,4-toluenediamine, vicinal toluenediamines, o-chloro-aniline, p-aminoaniline, 1,5-diaminonaphthalene, methylene dianiline, the various condensation products of aniline and formaldehyde, and the isomeric diaminotoluenes; and aliphatic amines such as mono-, di-, and trialkanolamines, ethylene diamine, propylene diamine, diethylenetriamine, methylamine, triisopropanolamine, 1,3-diaminopropane, 1,3-diaminobutane, and 1,4-diaminobutane. Preferable amines include monoethanolamine, vicinal toluenediamines, ethylenediamines, and propylenediamine.

[0043] Yet another class of polyether polyols contemplated for use in this disclosure are alkylene oxide adducts of a phenol/formaldehyde/alkanolamine

resin, frequently called "Mannich" polyols such as disclosed in U.S. Pat. Nos. 4,883,826; 4,939,182; and 5,120,815.

[0044] The amount of polyol to be used relative to the isocyanate normally should be such that the isocyanate groups are present in at least an equivalent amount, and preferably, in slight excess, compared to the free hydroxyl groups. In some embodiments, the components will be proportioned so as to provide from about 0.9 to about 1.5 mole equivalents of isocyanate groups per mole equivalent of hydroxyl groups. However, for certain foams the mole equivalents of isocyanate to hydroxyl groups can be as low as 0.4.

[0045] Also included in the foam composition is a blowing agent, which may be selected based in part upon the desired density of the final foam. In certain non-limiting embodiments hydrocarbon blowing agents may be selected. For example, hydrocarbon or fluorine-containing hydrohalocarbon blowing agents may be used, and in some instances may serve to reduce, or further reduce, viscosity, and thereby enhance processability. Among these are, for example, butane, isobutane, 2,3-dimethylbutane, n- and i-pentane isomers, hexane isomers, heptane isomers, cycloalkanes including cyclopentane, cyclohexane, cycloheptane, and combinations thereof, HFC-245fa (1,1,1,3,3-pentafluoropropane), HFC-365mfc (1,1,1,3,3-penta-fluorobutane), HFC-227ea (1,1,1,2,3,3,3-heptafluoropropane), HFC-134a (1,1,1,2-tetrafluoroethane), combinations of two or more of the above, and the like. In one particular embodiment, the blowing agent is an unsaturated halogenated hydroolefin such as a hydrofluoroolefin (HFO), hydrochlorofluoroolefin (HCFO), or mixtures thereof. Preferred hydrofluoroolefin (HFO) blowing agents contain 3, 4, 5, or 6 carbons, and include but are not limited to pentafluoropropenes, such as 1,2,3,3,3-pentafluoropropene (HFO-1225ye); tetrafluoropropenes, such as 1,3,3,3-tetrafluoropropene (HFO-1234ze, E and Z isomers), 2,3,3,3-tetrafluoropropene (HFO-1234yf), and 1,2,3,3-tetrafluoropropene (HFO-1234ye); trifluoropropenes, such as 3,3,3-trifluoropropene (HFO-1243zf);

tetrafluorobutenes, such as (HFO- 1345); pentafluorobutene isomers, such as (HFO-1354); hexafluorobutene isomers, such as (HFO-1336); heptafluorobutene isomers, such as (HFO-1327); heptafluoropentene isomers, such as (HFO-1447); octafluoropentene isomers, such as (HFO-1438); nonafluoropentene isomers, such as (HFO-1429); and hydrochlorofluoroolefins, such as 1-chloro-3,3,3-trifluoropropene (HCFO-1233zd) (E and Z isomers), 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf), HCFO-1223, 1,2-dichloro-1,2-difluoroethene (E and Z isomers), 3,3-dichloro-3-fluoropropene, 2-chloro-1,1,1,4,4,4-hexafluorobutene-2 (E and Z isomers), and 2-chloro-1,1,1,3,4,4,4-heptafluorobutene-2 (E and Z isomers). These hydrocarbons and/or non-fluorine-containing hydrohalocarbons may be used in an amount of about 0.5 parts by weight to about 30 parts by weight, or about 1 part by weight to about 10 parts by weight, based on 100 parts by weight of polyol(s).

[0046] Another blowing agent that may be used is formic acid or another carboxylic acid. The formic acid or other carboxylic acid may be used in an amount of from about 0.5 parts by weight to about 8 parts by weight, based on 100 parts by weight of polyol(s). It is also contemplated that other aliphatic mono- and polycarboxylic acids may be employed, such as those disclosed in U.S. Pat. No. 5,143,945, which is incorporated herein by reference in its entirety, and including isobutyric acid, ethylbutyric acid, ethylhexanoic acid, and combinations thereof.

[0047] In addition to, or in lieu of, the blowing agents above, water may also be optionally selected as a blowing agent. The water is, in some non-limiting embodiments, present in an amount of from about 0.1 parts by weight to about 40 parts by weight, or from about 0.15 parts by weight to about 20 parts by weight, or from about 0.25 parts by weight to about 5 parts by weight, or from about 0.5 parts by weight to about 3 parts by weight, based on 100 parts by weight of polyol(s). In some embodiments, when preparing a polyurethane or polyisocyanurate foam, in order to facilitate and give desirable processing

characteristics, the amount of water used may not exceed 3 parts by weight water, or not more than 2.5 parts by weight of water, or not more than 1 part by weight of water, based on 100 parts by weight of polyol(s). Omission of water may be desirable in some non-limiting embodiments.

[0048] In addition to the catalyst according to the present disclosure, other catalysts may optionally be included in the foam composition. In one embodiment, the additional catalyst(s) are also substantially free of nonylphenol.

[0049] According to another embodiment, an amine catalyst may be included, including any organic compound which contains at least one tertiary nitrogen atom and is capable of catalyzing the hydroxyl/isocyanate reaction between the isocyanate and polyol. Typical classes of amines include the N-alkylmorpholines, N-alkyl-alkanolamines, N,N-dialkylcyclohexylamines, and alkylamines where the alkyl groups are methyl, ethyl, propyl, butyl and isomeric forms thereof, and heterocyclic amines. Typical but non-limiting thereof are triethylenediamine, tetramethylethylenediamine, bis(2-dimethylaminoethyl)ether, triethylamine, tripropylamine, tributylamine, triamylamine, pyridine, quinoline, dimethylpiperazine, piperazine, N,N-dimethylcyclohexylamine, N-ethyl-morpholine, 2-methylpropanediamine, methyltriethyl-enediamine, 2,4,6-tridimethylamino-methyl)phenol, and mixtures thereof. The tertiary amines from which selection may be made may include bis(2-dimethylamino-ethyl)ether, dimethylcyclohexylamine, N,N-dimethyl-ethanolamine, triethylenediamine, triethylamine, 2,4,6-tri(dimethylaminomethyl)phenol, N,N',N-ethylmorpholine, and mixtures thereof.

[0050] Non-amine catalyst may also be included in foam compositions of the present disclosure. Typical of such catalysts are organometallic compounds of bismuth, lead, tin, titanium, iron, antimony, uranium, cadmium, cobalt, thorium, aluminum, mercury, zinc, nickel, cerium, molybdenum, vanadium, copper, manganese, zirconium, and combinations thereof. Included for illustrative

purposes only are bismuth nitrate, lead 2-ethylhexoate, lead benzoate, lead naphthenate, ferric chloride, antimony trichloride, antimony glycolate, combinations thereof, and the like. Embodiments include the stannous salts of carboxylic acids, such as stannous acetate, stannous octoate, stannous 2-ethylhexoate, 1-methylimidazole, and stannous laurate, as well as the dialkyl tin salts of carboxylic acids, such as dibutyl tin diacetate, dibutyl tin dilaurate, dibutyl tin dimaleate, dioctyl tin diacetate, combinations thereof and the like.

[0051] The amount of catalyst of the present disclosure (and optional catalyst(s)) added to the foam composition is a catalytically sufficient amount. In one embodiment, the amount of catalyst of the present disclosure (and optional catalyst(s)) that is included in the foam composition is from about 0.5 parts by weight to about 15 parts by weight, in another embodiment from about 0.75 part by weight to about 12 parts by weight, and in still another embodiment from about 1 part by weight to about 10 parts by weight, based on 100 parts by weight of polyol(s).

[0052] If desired, the foam composition can also comprise additives. Examples include: cell stabilizers, such as organopolysiloxane surfactants; flame retardants such as halogenated organophosphorous compounds; chain extenders such as ethylene glycol and butane diol; crosslinkers such as glycerol, trimethylolpropane, pentaerythritol, sucrose, sorbitol, or mixtures thereof; fillers and pigments, such as calcium carbonate, titanium dioxide, iron oxide, chromium oxide, azo/diazo dyes, phthalocyanines, dioxazines, carbon black barium sulfate, graphite, microspheres, alumina trihydrate, wollastonite, prepared glass fibers (dropped or continuous), and polyester fibers and other polymeric fibers, as well as various combinations thereof; odor masks, biocides, antioxidants, UV stabilizers such as hydroxybenzotriazoles, zinc dibutyl thiocarbamate, 2,6-ditertiarybutyl catechol, hydroxybenzophenones, hindered amines and phosphites; antistatic agents; viscosity modifiers and combinations thereof.

[0053] Each additive, except fillers and pigments, may constitute from 0.01 parts by weight to about 10 parts by weight, based on 100 parts by weight of polyol(s). Fillers and pigments may be used in quantities as high as up to about 50 parts by weight, based on 100 parts by weight of polyol(s).

[0054] The preparation of polyurethane or polyisocyanurate foams using the foam compositions described herein may follow any of the methods well known in the art for preparing polyurethane and polyisocyanurate foam, for example, as described in Saunders and Frisch, "Volumes I and II Polyurethanes Chemistry and Technology" (1962, John Wiley and Sons, New York, N.Y.), or Gum et al., "Reaction Polymers" (1992, Oxford University Press, New York, N.Y.), or Klempner and Sendijarevic, "Polymeric Foams and Foam Technology" (2004, Hanser Gardner Publications, Cincinnati, Ohio). In general, the various components are brought together and mixed using manual or mechanical mixing means to form the foam. Generally, the polyol and catalyst are preblended to form a single component which is fed as one stream to a conventional mixing head and admixed with the isocyanate which is fed as a separate stream to the mixing head. The blowing agent can be fed as a separate stream to the mixing head or blended with one or other, or both, of the other components prior to feeding the latter to the mixing head. The foams subsequently produced can be rigid, flexible, or semi-rigid, and can have a closed cell structure, an open cell structure or a mixture of open and closed cells and may vary in density of from about 0.5 pounds per cubic foot to about 60 pounds per cubic foot, such as from about 1.0 to 20.0 pounds per cubic foot, and in other embodiments from about 1.5 to 6.0 pounds per cubic foot. The foams are suitable for use in a wide range of applications including appliance insulation (for e.g., insulating refrigerators or water heaters), structural insulation (for e.g. spray foams or lamination foams for commercial or residential insulation), cushioning, flotation, packaging, adhesives, void filling, crafts and decorative, and shock absorption.

[0055] In one particular embodiment, the polyurethane or polyisocyanurate foam prepared according to the process of this disclosure is a rigid, closed-cell foam. Such foam is typically prepared by intimately mixing the reaction components, for example, a B-side containing a polyol/blowing agent/catalyst according to the present disclosure and an A-side containing an isocyanate (i.e. two streams); or a B-side containing a polyol/blowing agent, a C-side containing the catalyst according to the present disclosure, and an A-side containing a polyisocyanate component (at least three streams, wherein the polyol/blowing agent and catalyst according to the present disclosure mix just prior to contact thereof with the polyisocyanate component) at room temperature or at a slightly elevated temperature for a short period of time. Mixing of streams may be carried out either in a spray apparatus, a mixhead with or without a static mixer, or a vessel. The mixture is then sprayed or otherwise deposited onto a substrate. This substrate may be, for example, a rigid or flexible facing sheet made of foil or another material, including another layer of similar or dissimilar polyurethane or polyisocyanurate which is being conveyed, continuously or discontinuously, along a production line, or directly onto a conveyor belt.

[0056] In alternative embodiments the mixture may be poured into an open mold or distributed via laydown equipment into an open mold or simply deposited at or into a location for which it is destined, i.e., a pour-in-place application, such as between the interior and exterior walls of a structure. In the case of deposition on a facing sheet, a second sheet may be applied on top of the deposited mixture. In other embodiments, the mixture may be injected into a closed mold, with or without vacuum assistance for cavity-filling. If a mold is employed, it is most typically heated.

[0057] In general, such applications above may be accomplished using the known one-shot, prepolymer or semi-prepolymer techniques used together with conventional mixing methods. The mixture, on reacting, takes the shape of the mold or adheres to the substrate to produce a polyurethane or polyisocyanurate

foam of a more-or-less predefined structure, which is then allowed to cure in place or in the mold, either partially or fully. Suitable conditions for promoting the curing include a temperature of typically from 20°C to 150°C, such as from 35°C to 75°C, and including from 45°C to 55°C. Such temperatures will usually permit the sufficiently cured foam to be removed from the mold, where such is used, typically within from about 1 to 10 minutes and more typically within from 1 to 5 minutes after mixing of the reactants. Optimum cure conditions will depend upon the particular components, including catalysts and quantities used in preparing the foam and also the size and shape of the article manufactured.

[0058] The result may be a rigid foam in the form of slabstock, a molding, a filled cavity, including but not limited to a pipe or insulated wall or hull structure, a sprayed foam, a frothed foam, or a continuously- or discontinuously-manufactured laminate product, including but not limited to a laminate or laminated product formed with other materials, such as hardboard, plasterboard, plastics, paper, metal, or a combination thereof.

EXAMPLES

[0059] Example 1. Preparation of Inventive Catalyst.

The following components were added to a 1000 ml flask equipped with a heating mantle, temperature controller, nitrogen sparge tube, K head, condenser, mixer and receiver:

Sodium Glycinate, 50% water	192 grams
Diethylene glycol	225 grams
Formaldehyde, 55%	52.4 grams

The contents were heated to 85°C and then held at that temperature for one hour. The temperature was then increased to 105°C to remove water and methanol.

348.37 grams of a light brown mobile liquid were obtained and NMR confirmed the presence of a sodium glycinate triazine structure.

[0060] Example 2. Preparation of Inventive Catalyst.

To the apparatus described in example #1 were added:

Water, deionized	300 grams
Glycine	47.5 grams
Potassium Hydroxide, 45%	81.04 grams
Formaldehyde 55%	33.31 grams

The contents were heated to 80-100°C for one hour and the temperature was then slowly increased to 110°C to remove water and methanol. 173.43 grams of product were obtained and FTIR and NMR scans of the product confirmed the presence of a potassium aminoacetate triazine structure.

[0061] Example 3. Foam Preparation.

Foams were prepared from the following components:

A-Side

Component	Example 3A	Example 3B	Example 3C
Polyisocyanate[1]	44.4 g	44.4 g	44.4 g

[1] Rubinate® M polyisocyanate.

B-Side

Component	3A	3B	3C
Polyol A[1]	22.75 g	22.75 g	22.75 g

Component	3A	3B	3C
Polyol B[2]	22.75 g	22.75 g	22.75 g
Water	0.27 g	0.27 g	0.27 g
Blowing Agent[3]	8.67 g	8.67 g	8.67 g
Surfactant[4]	0.81 g	0.81 g	0.81 g
State of the art Catalyst[5]	6.0 g		
Inventive Catalyst[6]		6.0 g	
Inventive Catalyst[7]			12 g

[1] JEFFOL®SD-361 polyol, a sucrose diethylene glycol initiated PO polyol adduct.

[2] JEFFOL®FX31-240 polyol, a glycerol initiated PO polyol adduct.

[3] Hydrofluorocarbon 141b.

[4] Tegostab® B 8404 silicone surfactant.

[5] JEFFCAT® TR-52 catalyst, a Mannich condensate prepared from nonylphenol.

[6] Example 2 catalyst.

[7] Example 1 catalyst.

The catalyst was added to the B-side and mixed for 10 seconds. The A-side and B-side were then mixed together for 10 seconds to produce foams having the following properties:

Property	3A	3B	3C
Cream Time (sec)	20	19	37
Top of Cup (sec)	40	39	79
String Gel (sec)	49	49	90
Tack Free Time (sec)	65	62	140
End of Rise (sec)	90	85	167

[0062] Example 4. Foam Preparation

Foams were prepared from the following components:

A-Side

Component	Example 4A	Example 4B	Example 4C
Polyisocyanate[1]	218.5 g	218.5 g	218.5 g

[1] Rubinate® 1850 polyisocyanate.

B-Side

Component	4A	4B	4C
Polyol A[1]	100 g	100 g	100 g
Water	0.27 g	0.27 g	0.27 g
Blowing Agent[2]	26.4 g	26.4 g	26.4 g
Surfactant[3]	2 g	2 g	2 g
Fire Retardant[4]	9 g	9 g	9 g
Fire Retardant[5]	13 g	13 g	13 g
State of the art Catalyst[6]	1.45 g	1.45 g	1.45 g
State of the art Catalyst[7]	5.34 g	5.34 g	
State of the art Catalyst[8]	1.35 g		1.35 g
State of the art Catalyst[9]	0.67 g	0.67 g	0.67 g
Inventive Catalyst[10]		1.35 g	1.35 g

[1] STEPANOL®2352 polyol, an aromatic polyester polyol.

[2] N-pentane.

[3] Tegostab® B 8491 silicone surfactant.

[4] RB-79, a tetrabromophthalic anhydride ester.

[5] TCPP, tris-chloropropylphosphate.

[6] Pelcat 9648A, potassium acetate in ethylene glycol.

[7] Pelcat 9540A, potassium octoate in diethylene glycol.

[8] JEFFCAT® TR-52 catalyst, a Mannich condensate prepared from nonylphenol.

[9] JEFFCAT® Z-20 catalyst, bis-dimethylaminoethylether.

[10] Example 2 catalyst.

The catalyst was added to the B-side and mixed for 10 seconds. The A-side and B-side were then mixed together at a 60:40 ratio to produce foams having the following properties:

Property	4A	4B	4C
Cream Time (sec)	6	6	6
Top of Cup (sec)	10	9	13
String Gel (sec)	18	18	29
Tack Free Time (sec)	26	22	41
End of Rise (sec)	34	33	47
Firm Time (sec)	45	43	70

The inventive catalyst allows for a similar reaction profile as the state of the art catalyst, but does not contain nonylphenol.

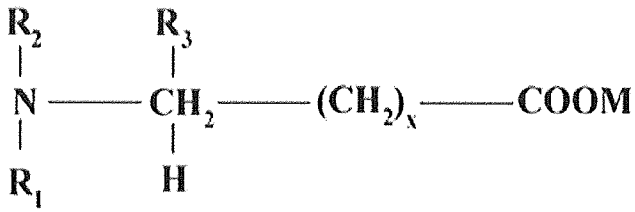
[0063] While the foregoing is directed to embodiments of the present disclosure, other and further embodiments of the disclosure may be devised without departing from the basic scope thereof, and the scope thereof is determined by the claims that follow.

Claims:

1. A catalyst comprising a reaction product of: (i) an aldehyde; and (ii) a metal salt of an aminocarboxylic acid.

2. The catalyst according to claim 1, wherein the aldehyde is formaldehyde.

3. The catalyst according to claim 1, wherein the metal salt of an aminocarboxylic acid is a compound of the formula



where R_1, R_2, and R_3 are, independently of one another, H or a C_1-C_3 alkyl group, M is sodium or potassium and x is an integer from 0 to 5.

4. The catalyst according to claim 3, wherein x is 0.

5. The catalyst according to claim 1, wherein the metal salt of an aminocarboxylic acid is a sodium salt of N-methylglycine or a potassium salt of N-methylglycine.

6. The catalyst according to claim 1, wherein the metal salt of the aminocarboxylic acid is a sodium salt of glycine or a potassium salt of glycine.

7. A polyurethane or polyisocyanurate foam composition comprising a polyisocyanate, a polyol, a blowing agent and the catalyst according to claim 1.

8. The polyurethane or polyisocyanurate foam composition according to claim 7, further comprising an additional catalyst wherein the additional catalyst is substantially free of nonylphenol.

9. The polyurethane or polyisocyanurate foam composition according to claim 7, further comprising at least one cell stabilizer, flame retardant, chain extender, crosslinker, filler, pigment, odor mask, biocide, antioxidant, UV stabilizer, antistatic agent or viscosity modifier.

10. A process for preparing a polyurethane or polyisocyanurate foam comprising contacting a polyisocyanate, polyol, blowing agent and the catalyst according to claim 1.

11. A foam obtained from the process of claim 10.

12. The foam according to claim 11, wherein the foam is a rigid foam in the form of slabstock, a molding, a filled cavity, a sprayed foam, a frothed foam, or a continuously- or discontinuously-manufactured laminate product.

13. A process for preparing a catalyst comprising the step of reacting an aldehyde and a metal salt of an aminocarboxylic acid at a temperature from 0°C to 80°C.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 16/66454

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - C08L 75/04; C08G 18/02; C07D 251/04 (2017.01)
CPC - C08J2375/04; C08J2205/10; C18G18/225
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC(8): C08L 75/04; C08G 18/02; C07D 251/04 (2017.01)
CPC: C08J2375/04; C08J2205/10; C18G18/225

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC: 525/395

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PatBase, Google Scholar, PubWEST
polyurethane/polyisocyanurate, foam, catalyst, amino acid triazine, N-methylglycine, formaldehyde reaction product, polyol, blowing agent

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,310,633 A (HAAS et al.) 12 January 1982 (12.01.1982) col 1, ln 34 to col 2, ln 25; col 2, ln 17-20; col 5, ln 49-54	1-4, 6-13
X	US 3,896,052 A (LOCKWOOD et al.) 22 July 1975 (22.07.1975) col 2, ln 15-40; col 6, ln 16-63, scheme; col 7, ln 15-27; col 15, ln 10-16, Example 1; col 16, ln 25-62, Example 8	1, 5
A	US 4,546,122 A (RADOVICH et al.) 08 October 1985 (08.10.1985) Entire Document	1-13
A	US 8,269,044 B2 (TAKANO et al.) 18 September 2012 (18.09.2012) Entire Document	1-13
A	US 2009/0317627 A1 (TSAI et al.) 24 December 2009 (24.12.2009) Entire Document	1-13
A	US 5,347,004 A (RIVERS et al.) 13 September 1994 (13.09.1994) Entire Document	1-13

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

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14 February 2017	27 MAR 2017

Name and mailing address of the ISA/US	Authorized officer:
Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774