REDUCED EMISSIONS LOW DENSITY SPRAY POLYURETHANE FOAM

MOUSSE POLYURÉTHANE PROJETÉE CARACTÉRISÉE PAR UNE FAIBLE DENSITÉ ET DES ÉMISSIONS RÉDUITES
This disclosure relates to the production of low density polyurethane foam with low or no amine emissions, particularly full water blown spray polyurethane foams.

BACKGROUND OF THE INVENTION

Examples include HFO (hydrofluoroolefins), FO (fluoroolefins), CFO (chlorofluoroolefins) and HCFO (hydrochlorofluoroolefins) all of which are characterized in having low life in the environment resulting in low ODP as well as low GWP. CFCs can be conveniently replaced by hydrofluorocarbons (HFCs) which have lower ODP than CFCs. Another alternative is to use blowing agents that still contain chlorine however their ozone depletion potential (ODP) is lower than those of CFCs due to their shorter life in the environment. Some other alternatives are now currently available or under development. For example HCFCs are substituents that contain chlorine but have low life in the environment with respect to ODP and GWP. Alternatives include hydrochlorofluorocarbons (HCFCs) as an interim solution. HCFCs are substances that still contain chlorine however their ozone depletion potential (ODP) is lower than those of CFCs due to their shorter life in the environment. Other alternatives include HFO (hydrofluoroolefins), FO (fluoroolefins), CFO (chlorofluoroolefins) and HCFO (hydrochlorofluoroolefins) all of which are characterized in having low life in the environment resulting in low ODP as well as low GWP. Examples include trans-1,3,3,3-tetrafluoroprop-1-ene or HFO-1234ze; tran-1-chloro-3,3,3-trifluoropropene or HCFO-1233zd; 2,3,3,3-tetrafluoropropene or HFO-1234yf, mixtures thereof and similar structures. However, these blowing agents are relatively expensive when compared with other available materials such as acetone or carbon dioxide. The most convenient route for blowing polyurethane polymers is by in-situ generation of carbon dioxide when isocyanates react with water.

BRIEF SUMMARY OF THE INVENTION

The industry needs amine catalysts that can effectively increase the rate of rise kinetics of low density full water-blown foam to avoid foam "creep" during spraying while at the same time maintain good physical properties, reduce odor, eliminate emissions and provide reactive systems that can minimize the exposure of workers and end users to the risk of glaucoma. Foam "creep" is an expression used to describe a visual observation of a downward flow of polyurethane polymer caused by gravity when the polymerizing mass is not increasing its viscosity sufficiently fast due to low catalytic activity.
The objective of this invention is to provide a catalyst composition that is capable of providing a similar performance to the standard technology based on BDMAEE with the additional benefit of reduced emissions, odor and reduced amine exposure.

Another objective is to provide a catalyst composition that is able to provide fast reaction kinetics with the benefit of no post cure amine emissions even at temperatures as high as 120°C.

Yet another objective of this disclosure is to provide a polyurethane foam formula that produces polyurethane foams with low to no amine emission, but have similar physical and mechanical properties as those obtained with the current emissive amine catalyst standard BDMAEE.

In one exemplary embodiment, the current disclosure provides a catalyst composition for catalyzing the formation of polyurethane foam. The catalyst composition comprises at least one non-emissive catalyst and a tetraalkyl guanidine of the general formula:

\[
\begin{align*}
\text{N} & \quad \text{N} \\
R_1 & \quad R_2 \\
 & \quad R_3 \\
 & \quad R_4
\end{align*}
\]

Wherein \( R_1, R_2, R_3 \) and \( R_4 \) are independently C1-C10 alkyl groups and branched or un-branched isomers thereof, wherein the at least one non-emissive catalyst comprises bis(dimethylaminopropyl) amine and a compound selected from the group of N-(dimethylaminoethyl)- N-(2-hydroxyethyl)-N-methylamine, 2-[N-(dimethylaminoethoxyethyl)-N-methylamino] ethanol, and N,N,N'-trimethyl-N'-3-aminopropyl-bis(amoenoethyl) ether.

In another exemplary embodiment, a catalyst composition for catalyzing the formation of polyurethane foam is provided. The catalyst composition consists essentially of at least one non-emissive catalyst and a tetraalkyl guanidine of the general formula:

\[
\begin{align*}
\text{N} & \quad \text{N} \\
R_1 & \quad R_2 \\
 & \quad R_3 \\
 & \quad R_4
\end{align*}
\]

For the purpose of this disclosure, "consists essentially of" means that less than 5% by weight of the total catalyst composition comprises other emissive catalysts, metallic catalyst, additives or impurities. Examples of emissive catalysts include tertiary amines that do not have isocyanate-reactive functional groups. Preferred embodiments of the catalyst composition are described in claims 3 to 8.

The present invention further provides a catalyst composition for catalyzing the formation of polyurethane foam comprising 70% or more by weight of N,N,N'-trimethyl-N'-3-aminopropyl-bis(amoenoethyl) ether and 30% or less by weight of tetramethyl guanidine.

For the purpose of this disclosure, "consists essentially of" means that less than 5% by weight of the total catalyst composition comprises other emissive catalysts, metallic catalyst, additives or impurities. Examples of emissive catalysts include tertiary amines that do not have isocyanate-reactive functional groups. Preferred embodiments of the catalyst composition are described in claims 3 to 8.

The method may be carried out through means well-known to the skilled person in the art, such as a one-shot process as described in Dow Polyurethane: Flexible Foams by Ron Herrington and Kathy Hock.

In yet another exemplary embodiment, a polyurethane foam formulation is disclosed. Such formulation comprises at least one polyol, at least an isocyanate, an effective amount of a blowing agent composition, and an effective amount of a catalyst composition according to the invention.

The method may be carried out through means well-known to the skilled person in the art, such as a one-shot process as described in Dow Polyurethane: Flexible Foams by Ron Herrington and Kathy Hock.
sifiers, flame retardants, crosslinkers, cell stabilizers and any combination thereof.

[0021] The embodiments and various aspects of the invention can be used alone or in combination.

DETAILED DESCRIPTION OF THE INVENTION

[0022] The instant invention relates to compositions and methods to make low density and low or no-amine emissions foams using reactive catalyst. The method is useful in the preparation of 6 Kg/m³ to 16 Kg/m³ density foam, particularly 8 Kg/m³ density foam, using water as the main blowing agent. Water is able to react with isocyanates in the presence of tertiary amines to produce carbon dioxide that acts as blowing agent. This type of low density foam grade is conventionally made using strong blowing catalysts such as bis-(dimethylaminomethyl)-ether (BDMAEE, commercially available from Air Products and Chemicals as DABCO®BL19 or DABCO®BL11) or pentamethyl-diethylenetriamine (PMDETA, available from Air Products as POLYCAT®5). However, a high level of amine emissions occurs during and after foam application because large amount of catalyst is required for reacting water with isocyanate in the blowing process. These emissions are a safety hazard because workers exposed to volatile amines can develop a medical condition known as glaucoma which is characterized by a temporary disturbance of vision. Workers’ exposure can be particularly severe in residential spraying of confined spaces due to the lack of sufficient ventilation. Exposure to amines can also occur during blending of the amines with other components of the polyurethane formulation as well as during occupancy of the sprayed residence.

[0023] The instant invention is free or substantially free of amine emissions. That is, no amine catalyst emissions were detected when foam volatiles were extracted by passing a constant flow of inert gas through a sample of polyurethane foam that was conditioned at 32°C and 60°C. Furthermore, foam emissions were evaluated using a more severe test method called VDA278 typically used in automotive applications in which foam samples are extracted at 90°C and 120°C. Thermal desorption method VDA 278 is a standard polyurethane foam emission test procedure used in the automotive industry to evaluate emissions from polyurethane foam under aggressive conditions. In a dynamic headspace experiment, gas extraction is carried out continuously to remove all volatile components from the foam sample. The method consists essentially of two steps, where gaseous emissions that typically contribute to the contamination of the interior air quality are measured at 90°C for 30 minutes (VOC) and subsequently at 120°C for 60 minutes. In the first step, the foam sample is put into a thermal desorption tube that is continuously flushed with an inert gas for 30 minutes at 90°C. The volatile emissions being released from foam are collected in a cryogenic trap at-150°C and at the end of the period the trapped residue is heated to 280°C and injected into a GC-MS analyzer. Once the VOC’s are measured, the second step consists of measuring the condensable emissions that are responsible for fogging in cars (FOG). The same sample is now heated up to 120°C and gas is passed through the sample for 60 minutes, while the volatiles are condensed in a cryogenic trap at 150°C. The condensates are then heated up to 280°C and analyzed by GC-MS.

[0024] The instant invention also relates to a result that acceleration of the front end of the rate of rise profile can happen when conventional gelling and/or blowing amine catalyst are combined with a tetramethylguanidine such as tetramethylguanidine at less or 40 weight percent of the total amine content present in the high water formulation, or at less or 5% by weight of the total catalyst composition. This result is unexpected because tetramethyl guanidine is not structurally related to BDMAEE and, therefore, it is not expected to substantially activate the isocyanate/water reaction.

[0025] For the purpose of this disclosure, “non-emissive catalyst” is meant to be gelling and blowing amine catalysts having isocyanate reactive functionalities such as primary and secondary hydroxyl group (-OH), primary and secondary amine groups, urea and alkyl (substituted or unsubstituted) ureas and amides. Examples of catalysts comprise bis-(N,N-dimethylaminopropyl)-amine (commercially available from Air Products and Chemicals as POLYCAT®15), N,N,N′-trimethylaminoethyl-ethanolamine (commercially available from Air Products and Chemicals as DABCO®T), POLYCAT-17 (N,N-dimethylaminopropyl-N′-methyl-N)-(2-hydroxyethyl)amine, dimethylethanolamine (commercially available as DABCO® DMEA), N,N-bis(3-dimethylamino-propyl)-N-(2-hydroxypropyl) amine, N,N-dimethyl-N′,N′-bis(2-hydroxypropyl)-1,3-propylenediamine, 2-(2-dimethylaminoethyl)ethanol, dimethylinopropylurea and bis(dimethylaminopropyl)urea (commercially available as DABCO®NE1070 and DABCO®NE1080 from Air Products and Chemicals), 2-[N-(dimethylaminomethoxyethyl)-(N-methylamino] ethanol, N,N,N′-trimethyl-N′-3-aminopropyl-bis(aminoethyl) ether, dimethylaminopropylamine (DMAPA); N-methyl-N-2-hydroxypropyl-piperazine, bis(dimethylamino)-2-propanol, N-(3-aminopropyl)imidazole, N-(2-hydroxypropyl)imidazol, 6-dimethylamino-1-hexanol and mixtures thereof. The amount of non-emissive catalyst typically ranges from 10 pphp to 50 pphp and in some cases, 5 pphp to 60 pphp.

[0026] The catalyst composition of the instant invention may comprise one or more non-emissive catalyst as defined above in combination with one or more tetraalkyl guanidine of the general formula:
wherein R1, R2, R3 and R4 are independently C1-C10 alkyl groups. Unless otherwise specified, alkyl groups described herein are intended to include all structural isomers, linear or branched, of a given moiety within this definition. As an example, unless otherwise specified, the term propyl is meant to include n-propyl and iso-propyl, while the term butyl is meant to include n-butyl, iso-butyl, t-butyl, sec-butyl, and so forth. For instance, non-limiting examples of octyl isomers include 2-ethyl hexyl and neoctyl. An example of a suitable tetraalkyl guanidine is tetramethyl guanidine. The amount of tetraalkyl guanidine can range from 0.5 pphp to 20 pphp and normally 1.0 pphp to 10 pphp.

[0027] In an alternative embodiment, the catalyst composition of the instant invention may consist essentially of one or more non-emissive catalyst in combination with one or more tetraalkyl guanidine. By way of "consisting essentially of", the catalyst composition has less than 10 % by weight of emissive amine catalyst, metallic catalyst, other additives or impurities and typically 5 wt.% or less of the foregoing emissive catalysts. Emissive amine catalyst comprises tertiary amine that does not have any isocyanate-reactive functionality. Examples of emissive amine catalyst comprise tertiary amines that are highly volatile and without isocyanate-reactive groups such as, diazabicyclooctane (triethylene diamine), supplied commercially as DABCO 33-L® catalyst, tris(dimethylaminopropyl) amine (Polycat® 9), dimethylaminoclohexylamine (Polycat® 8) and bis(dimethylaminopropyl)-N-methylamine (Polycat® 77). Suitable volatile blowing catalysts include, for example, bis-dimethylaminoethyl ether, commercially supplied as DABCO® BL-11 catalyst by Air Products and Chemicals, Inc.; as well as pentamethyldiethylenetriamine (POLYCAT® 5, Air Products and Chemicals, Inc.) and related compounds; higher peralkylated polyamines; 2-[N-(dimethylaminoethoxyethyl)]-N-methylaminoethanol and related structures; alkoxylated polyamines; imidazole-boron compositions; or amino propyl-bis(aminoethyl)ether compositions. Examples of metallic catalyst include tin(II) carboxylate salts, dialkyltin dicarboxylate salts such as dibutyltin dilaurate, dimethyltin dilaurate, dimethyltin diacetate, dibutyltin diacetate, dimethyltin dialuurymercaptide, dibutyltin dilaurylmercaptide, dimethyltin disoctylmalate, dibutyltin disoctylmalate, dimethyltin bis(2-thylhexyl mercaptacetate), dibutyltin bis(2-thylhexyl mercaptacetate), stannous octate, other suitable organotin catalysts, or a combination thereof. Other metals can also be included, such as, for example, bismuth (Bi). Suitable bismuth and tin (II) carboxylate salts includes salts of pentanoic acid, neopentanoic acid, hexanoic acid, 2-ethylhexyl carboxylic acid, neohexanoic acid, octanoic acid, neooctanoic acid, heptanoic acid, neoheptanoic acid, nonanoic acid, isononanoic acid, neononanoic acid, decanoic acid, neodecanoic acid, undecanoic acid, dodecanoic acid, neodecanoic acid, and other suitable carboxylic acids. Other salts of transition metals of lead (Pb), iron (Fe), zinc (Zn) with pentanoic acid, neopentanoic acid, hexanoic acid, 2-ethylhexyl carboxylic acid, octanoic acid, neooctanoic acid, neoheptanoic acid, neodecanoic acid, and other suitable carboxylic acids may also be included.

[0028] Depending upon the requirements during foam manufacturing or for the end-use application of the foam product, various additives can be employed in the PUR foam formulation to tailor specific properties. These include, but are not limited to, cell openers, cell stabilizers, emulsifiers, flame retardants, chain extenders, epoxy resins, acrylic resins, fillers, pigments, or any combination thereof. The total amount of the combined additives can range from 50 pphp to 250 pphp and typically 90pphp to 200 pphp. It is understood that other mixtures or materials that are known in the art can be included in the foam formulations and are within the scope of the present invention.

[0029] The catalyst composition of this disclosure is suitable for polyurethane formulation containing water as the sole blowing agent. Alternatively, the catalyst composition may be used with a blowing agent composition comprising water and any blowing agent known in the art. Suitable blowing agents include compounds with low boiling points which are vaporized during the exothermic polymerization reaction. Such blowing agents are generally inert or they have low reactivity and therefore it is likely that they will not decompose or react during the polymerization reaction. Examples of inert blowing agents include, but are not limited to, carbon dioxide, chlorofluorocarbons (CFCs), hydrofluorocarbons (HFCs), hydrochlorofluorocarbons (HCFCs), fluoroolefins (FOs), chlorofluoroolefins (CFOs), hydrofluoroolefins (HFOs), hydrochlorofluoroolefins (HCFOs), acetone, and low-boiling hydrocarbons such as cyclopentane, isopentane, n-pentane, and their mixtures. Other suitable blowing agents include compounds, for example water, that react with isocyanate compounds to produce carbon dioxide. The amount of blowing agent can range from 150 pphp to 20 pphp and typically 100 pphp to 40 pphp.

[0030] An exemplary embodiment of the catalyst composition comprises 70% or more by weight of N,N,N’-trimethyl-N’-3-aminopropyl-bis(aminoethyl) ether and 30% or less by weight of tetramethyl guanidine.
Polyurethane foams were prepared and tested in a conventional manner using the formulations shown below. The following formulation was used to test foams and study the rate of rise kinetics:

<table>
<thead>
<tr>
<th>Components</th>
<th>PPHP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyether Polyol</td>
<td>100</td>
</tr>
<tr>
<td>Emulsifier</td>
<td>32</td>
</tr>
<tr>
<td>Flame Retardant (TCPP)</td>
<td>77</td>
</tr>
<tr>
<td>Surfactant</td>
<td>3.4</td>
</tr>
<tr>
<td>Cell Opener</td>
<td>0.15</td>
</tr>
<tr>
<td>DABCO®BL-11 (BDMAEE)</td>
<td>10</td>
</tr>
<tr>
<td>Water</td>
<td>60</td>
</tr>
</tbody>
</table>

The PUR formulation comprising polyether polyol, water, cell stabilizers such as silicon surfactants, emulsifiers, flame retardants and optionally cell openers are combined with the catalyst composition of this disclosure.

Polyols suitable for use in such PUR formulations comprise active hydrogen-containing compounds for use with the foregoing polyisocyanates in forming the polyurethane foams of this invention can be any of those organic compounds having at least two hydroxyl groups such as, for example, polyols. Polyols that are typically used in PUR foam formation processes include polyalkylene ether and polyester polyols. The polyalkylene ether polyol includes the poly(alkyleneoxide) polymers such as poly(ethyleneoxide) and poly(propyleneoxide) polymers and copolymers with terminal hydroxyl groups derived from polyhydric compounds, including diols and triols. These include, but are not limited to, ethylene glycol, propylene glycol, 1,3-butane diol, 1,4-butane diol, 1,6-hexane diol, neopentyl glycol, diethylene glycol, dipropylene glycol, pentaerythritol, glycerol, diglycerol, trimethylol propane, cyclohexane diol, and sugars such as sucrose and like low molecular weight polyols.

Amine polyether polyols can be used in the present invention. These can be prepared when an amine such as, for example, ethylenediamine, diethylenetriamine, tolylenediamine, diphenylmethanediamine, or triethanolamine is reacted with ethylene oxide or propylene oxide.

In another aspect of the present invention, a single high molecular weight polyether polyol, or a mixture of high molecular weight polyether polyols, such as mixtures of different multifunctional materials and/or different molecular weight or different chemical composition materials can be used.

In yet another aspect of the present invention, polyester polyols can be used, including those produced when a dicarboxylic acid is reacted with an excess of a diol. Non-limiting examples include succinic, glutaric, pimelic, adipic, suberic, azelaic acid or phthalic acid or phthalic anhydride reacting with ethylene glycol or butanediol. Polyols useful in the present invention can be produced by reacting a lactone with an excess of a diol, for example, caprolactone reacted with propylene glycol. In a further aspect, active hydrogen-containing compounds such as polyester polyols and polyether polyols, and combinations thereof, are useful in the present invention.

Examples of emulsifiers that can be used in the instant invention can comprise nonylphenol ethoxylates, anionic emulsifiers such as salts of fatty acids, salts of sulfuric acid esters, salts of phosphoric acid esters, salts of sulfonic acids, and combinations of any of these. Suitable cationic emulsifiers include, but are not limited to quaternary ammonium salts (pH dependent or permanently charged) such as cetyl trimethylammonium chloride, cetyl pyridinium chloride, polyethoxylated tallow amine, benzalkonium chloride, benzethonium chloride. Suitable zwitterionic or amphoteric emulsifiers include but are not limited to sulfates, amino acids, imino acids, betaines and phosphates. Suitable non-ionic emulsifiers include but are not limited to fatty alcohols, polyoxyethylene glycol alkyl ethers, polyoxypropylene glycol alkyl ethers, glucoaldes (such as decyl, lauryl and octyl glucoaldes), polyoxyethylene glycol alkyl phenol ethers, glycol alkyl esters. The amount of emulsifiers can range from 2.0 pphp to 50.0 pphp.

Examples of cell-openers that can be used in the instant invention can comprise silicone surfactants, organic anionic, cationic, zwitterionic or nonionic surfactants. Examples of suitable silicone surfactants include, but are not limited to, polyalkylsiloxanes, polyoxyalkylene polyol-modified dimethyipolsiloxanes, alkylene glycol-modified dimethyipolsiloxanes, or any combination thereof. Suitable anionic surfactants include, but are not limited to, salts of fatty acids, salts of sulfuric acid esters, salts of phosphoric acid esters, salts of sulfonic acids, and combinations of any of these. Suitable cationic surfactants include, but are not limited to quaternary ammonium salts (pH dependent or permanently charged) such as cetyl trimethylammonium chloride, cetyl pyridinium chloride, polyethoxylated tallow amine,
In the various aspects of the invention, the blowing agent composition comprises at least 75 wt% water, at least 80 wt%, at least 85 wt% water, at least 90 wt% water or at least 95 wt% water. In the desired embodiment of the various aspects of the invention, the blowing agent composition comprises 100 wt% water.

Nevertheless, other blowing agents can be used in combination with the water in the PUR foam formation process and they include, but are not limited to, methylene chloride, acetone, chlorofluorocarbons (CFCs), hydrofluorocarbons (HFCs), hydrochlorofluorocarbons (HCFCs), hydrocarbons, fluoroolefins (FO), chlorofluoroolefins (CFO) and hydrochlorofluoroolefins (HCFO). Non-limiting examples of HFCs include HFC-245fa, HFC-134a, and HFC-365. Illustrative examples of HCFCs include HCFC-141b, HCFC-22, and HCFC-123. Exemplary hydrocarbons include n-pentane, isopentane, cyclopentane, or any combination thereof.

The amount of blowing agent composition used can vary based on, for example, the intended use and application of the foam product and the desired foam stiffness and density. In the foam formulation and method for preparing a rigid PUR foam of the present invention, the water-containing blowing agent composition is present in amounts from 10 to 80 parts by weight per hundred weight parts polyol (pphp), from 12 to 60 pphp, from 14 to 40 pphp, or from 16 to 25 pphp.

Depending upon the requirements during foam manufacturing or for the end-use application of the foam product, various additives can be employed in the PUR foam formulation to tailor specific properties. These include, but are not limited to, cell stabilizers, flame retardants, chain extenders, epoxy resins, acrylic resins, fillers, pigments, or any combination thereof. The amount of these additives can range from 50 pphp to 250 pphp. It is understood that other mixtures or materials that are known in the art can be included in the foam formulations and are within the scope of the present invention.

The spray polyurethane foam is produced by contacting this mixture with isocyanate using a polyurethane foam spray gun that allows impingement mixing.

Examples of suitable polyisocyanates are hexamethylene diisocyanate, isophorone disiocyanate, phenylene diisocyanate, toluene diisocyanate ("TDI"), 4, 4′-diphenyl methane diisocyanate ("MDI"). Especially suitable are 2,4- and 2,6-toluene diisocyanate individually or together as their commercially available mixtures. Other suitable mixtures of diisocyanates are those known commercially as "crude MDI" also known as PAPI, which contains 60 % of 4, 4′-diphenylmethane diisocyanate along with other isomer and analogous higher polyisocyanates. Also, suitable are pre-polymer mixtures of these polyisocyanates comprising a partially pre-reacted mixture of polyisocyanates and polyester or polyurethane polyol. The amount of polyisocyanate can range from 1 pphp to 100 pphp and typically 5 pphp to 50 pphp.

Suitable polyols are those polyols typically used in the art for making rigid PUR foam including the previously described polyalkylene ether and polyester polyols. Also, useful are amine polyether polyls which can be prepared when an amine, such as ethylenediamine, diethylenetriamine, tolylene diamine, diphenylmethane diamine, triethanolamine is reacted with ethylene oxide or propylene oxide. Mannich polyols are also used in spray foam formulation to increase the reactivity of the system. Mannich polyols are typically prepared by condensation of phenol with formaldehyde in the presence of hydroxyl containing amines such as diethanolamine, ethanolamine. In the practice of this invention, a single high molecular weight polyether polyl may also be used. Also, mixtures of high molecular weight polyether polyls such as mixtures of different multifunctional materials and/or different molecular weight or different chemical composition materials may be used. Useful polyether polyls include those produced when a dicarboxylic acid is reacted with an excess of a diol for example adipic acid or phthalic acid or phthalic anhydride with ethylene glycol or butanediol or reacting a lactone with an excess of a diol such as caprolactone with propylene glycol. In one aspect of the invention, a single high molecular weight polyether polyl may be used as the base polyl. Alternatively, a mixture of high molecular weight polyether polyls, for example, mixtures of di- and tri-functional materials and/or different molecular weight or different chemical composition materials may be used. Such di- and tri-functional materials include, but are not limited to polyethylene glycol, polypropylene glycol, glycerol-based polymer triols, trimethylolpropane-based polymer triols, and other similar compounds or mixtures. Polyurea modified polyls are formed by the reaction of a diisocyanate and a diol in the presence of a diol where the reaction proceeds at a rate governed by the reactivity of the diisocyanate and the diol. The amount of these materials can range from 50 pphp to 250 pphp. It is understood that other mixtures or materials that are known in the art can be included in the foam formulations and are within the scope of the present invention.

Other useful polyls may include polyalkylene carbonate-based polyols and polyphosphate-based polyols.

Other suitable polyols that can be used according to the invention include natural oil polyols or polyols obtained from renewable natural resources such as vegetable oils. Polyls useful in the preparation of polyurethane foam from inexpensive and renewable resources are highly desirable to minimize the depletion of fossil fuel and other non-sus-

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tangible resources. Natural oils consist of triglycerides of saturated and unsaturated fatty acids. One natural oil polyol is castor oil, a natural triglyceride of ricinoleic acid which is commonly used to make polyurethane foam even though it has certain limitations such as low hydroxyl content. Other natural oils need to be chemically modified to introduce sufficient hydroxyl content to make them useful in the production of polyurethane polymers. There are two chemically reactive sites that can be considered when attempting to modify natural oil or fat into a useful polyol: 1) the unsaturated sites (double bonds); and 2) the ester functionality. Unsaturated sites present in oil or fat can be hydroxylated via epoxidation followed by ring opening or hydroformylation followed by hydrogenation. Alternatively, trans-esterification can also be utilized to introduce OH groups in natural oil and fat. The chemical process for the preparation of natural polyols using epoxidation route involves a reaction mixture that requires epoxidized natural oil, a ring opening acid catalyst and a ring opener. Epoxidized natural oils include epoxidized plant-based oils (epoxidized vegetable oils) and epoxidized animal fats. The epoxidized natural oils may be fully or partially epoxidized and these oils include soybean oil, corn oil, sunflower oil, olive oil, canola oil, sesame oil, palm oil, rapeseed oil, tung oil, cotton seed oil, safflower oil, peanut oil, linseed oil and combinations thereof. Animal fats include fish, tallow and lard. These natural oils are triglycerides of fatty acids which may be saturated or unsaturated with various chain lengths from C12 to C24. These acids can be: 1) saturated: lauric, myristic, palmitic, steric, arachidic and lignoceric; 2) mono-unsaturated: palmitoleic, oleic, and 3) poly-unsaturated: linoleic, linolenic, arachidonic. Partially or fully epoxidized natural oil may be prepared when reacting peroxyacid under suitable reaction conditions. Examples of peroxyacids utilized in the epoxidation of oils have been described in WO 2006/116456 A1. Ring opening of the epoxidized oils with alcohols, water and other compounds having one or multiple nucleophilic groups can be used. Depending on the reaction conditions oligomerization of the epoxidized oil can also occur. Ring opening yields natural oil polyol that can be used for the manufacture of polyurethane products. In the hydroformylation/hydrogenation process, the oil is hydroformylated in a reactor filled with a hydrogen/carbon monoxide mixture in the presence of a suitable catalyst (typically cobalt or rhodium) to form an aldehyde which is hydrogenated in the presence of cobalt or nickel catalyst to form a polyol. Alternatively, polyol from natural oils and fats can be produced by trans-esterification with a suitable poly-hydroxyl containing substance using an alkali metal or alkali earth metal base or salt as a trans-esterification catalyst. Any natural oil or alternatively any partially hydrogenated oil can be used in the transesterification process. Examples of oils include but are not limited to soybean, corn, cottonseed, peanut, castor, sunflower, canola, rapeseed, safflower, fish, seal, palm, tung, olive oil or any blend. Any multifunctional hydroxyl compound can also be used such as lactose, maltose, raffinose, sucrose, sorbitol, xylitol, erythritol, mannitol, or any combination. The amount of polyol can range from 1 pphp (an additive polyol) to 100 pphp (a single polyol used) and typically 5 pphp (an additive polyol) to 100 pphp (a single polyol).

[0048] The catalyst composition and the method for preparing polyurethane foam of the present invention are useful in the formation of low density, rigid polyurethane foams. Such foams are generally produced with an Isocyanate Index, or NCO Index within a range of 20 to 100, or 20 to 50. NCO index is the actual amount of polysiocyanate used divided by the theoretically required stoichiometric amount of polyisocyanate required to react with all the active hydrogen in the reaction mixture, multiplied by 100. For purposes of the present disclosure, Isocyanate Index is represented by the equation: Isocyanate Index = (Eq NCO/ Eq of active hydrogen) x 100, wherein Eq NCO is the number of NCO functional groups in the polyisocyanate, and Eq of active hydrogen is the number of equivalent active hydrogen atoms.

[0049] Other typical components found in the polyurethane formulation include cell stabilizers surfactants such as organopolysiloxanes, emulsifying agents, cell openers, flame retardants such as halogenated organophosphorous compounds and chain extenders such as ethylene glycol and butane diol. The amount of such components can range from 50 pphp to 150 pphp and typically 70 pphp to 120 pphp.

[0050] The term “contacting” is used herein to describe means to bring components into contact with each other in any order, in any manner, and for any length of time. For example, the components can be contacted by blending or mixing. Further, contacting of any component can occur in the presence or absence of any other component of the compositions or formulations described herein. Still further, two or more of the components of the formulation described herein may react to form other components in composing the composition. Combining additional materials or components can be done by any method known to one of skill in the art.

**COMPARATIVE EXAMPLE 1**

*Rate of Rise of Foam Prepared with Standard Emissive Amine Catalyst Blend (BDMAEE and DMAEE)*

[0051] The following formulation was used to make foam using the industry standard catalysts combination bis-(dimethylaminooethyl)-ether (BDMAEE) and dimethylaminoethoxy ethanol (DMAEE).

<table>
<thead>
<tr>
<th>Components</th>
<th>Parts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyether Polyol</td>
<td>30.94</td>
</tr>
</tbody>
</table>
The above components were mixed and allowed cooling to about 5°C before mixing with the corresponding amount of isocyanates. Approximately 25 g of the above premix were mixed with 25 g of isocyanate (MDI) in a mechanical agitator in a two litter plastic container. Start time, rate of rise, foam height, speed of foam formation were measured using a FOMAT sonar detector (Ultrasonic Fan Sensor LR 2-40 PFT) placed right above the mixing container and measured for several minutes. The diagram and table below provide the foam kinetic data for the standard. The Sonar detector monitors the foaming process and automatically records the Choice Time (sec), which is the time that the foam reaches 80% of the maximum height; the Rise Time (sec), which is the time that the foam reaches 98% of the maximum height; the Maximum Height (mm), which is the highest point in the rate of rise profile; the Final Height (mm), which is the final height reached at the end of each measurement.

### Comparative Example 2

**Foam Rate of Rise of Comparison Between BMDAEE/DMAEE Control and TMG (Tetramethylguanidine [TMG])**

Foams were prepared in a similar manner as the previous example. Tetramethylguanidine was used at two different use levels as shown in the table below.

<table>
<thead>
<tr>
<th>Components</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyether Polyol</td>
<td>30.94</td>
</tr>
<tr>
<td>Emulsifier (same as above)</td>
<td>9.88</td>
</tr>
<tr>
<td>Flame Retardant (TCP) (same as above)</td>
<td>23.74</td>
</tr>
<tr>
<td>Surfactant (same as above)</td>
<td>1.05</td>
</tr>
<tr>
<td>Cell Opener (same as above)</td>
<td>0.05</td>
</tr>
<tr>
<td>TMG (Tetramethylguanidine)</td>
<td>2.50</td>
</tr>
<tr>
<td>Water</td>
<td>18.05</td>
</tr>
<tr>
<td>MDI</td>
<td>91.23</td>
</tr>
</tbody>
</table>

[0053] Data below shows that the kinetic of rate of rise for foam #2 is much lower than the control standard. Increasing the level of TMG as in foam #3 gave a much faster kinetic than #2 and more comparable to the industry standard.
However, increasing the level of TMG had a deep negative impact on foam height. Furthermore, the physical properties of foam made with TMG are very poor and foam degradation was immediately seen after foam curing. The complete lack of mechanical integrity of foam made with TMG prevented its use in any practical application.

### COMPARATIVE EXAMPLE 3

**Foam Rate of Rise Comparison Between BMDAEE/DMAEE Control and Non-Emissive Catalyst Combination “A” Poly-cat®-15/Dabco®-T**

This example shows a comparison between the standard catalyst composed of a mixture of BDMAEE/DMAEE and catalyst combination “A” of non-emissive catalysts that includes 85 % bis(dimethyldimethylamine) and 15 % N-(dimethylaminoethyl)-N-(2-hydroxyethyl)-N-methylamine (commercially available as Dabco®-T). It is clear from the graph below that the standard is significantly more active that the non-emissive catalyst combination. While the BDMAEE/DMAEE standard is used at 7.52 parts the non-emissive catalyst combination requires a much higher use level and even at 8.5 parts some small front end delay is still observed as evidenced by choice time and rise time. The low catalytic activity is due to a combination of factors including catalyst immobilization and ineffective water activation as compared with BDMAEE.

### COMPARATIVE EXAMPLE 4

**Foam Rate of Rise Comparison Between BMDAEE/DMAEE Control and Non-Emissive Catalyst Combination “B” Made with 2-[N-(dimethylaminoethoxyethyl)] ethanol and DMAEE**

In this example, 10.4 parts of a catalyst combination “B” having the following components: a) 2-[N-(dimethylaminoethoxyethyl)]-N-methylamino] ethanol (78 %) and b) DMAEE (22 %) was used to make polyurethane foam and its rate of rise kinetic compared with the control standard BDMAEE/DMAEE catalyst system. The tables below show the formulation using catalyst combination “B” as well as the foam kinetic data.

### Parameters and Data

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Control #1</th>
<th>#2</th>
<th>#3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Choice Time (80%H, seconds)</td>
<td>5.8</td>
<td>20</td>
<td>4.4</td>
</tr>
<tr>
<td>Rise Time (98% H, seconds)</td>
<td>6.7</td>
<td>22</td>
<td>5.2</td>
</tr>
<tr>
<td>Maximum Height (mm)</td>
<td>231</td>
<td>175</td>
<td>175</td>
</tr>
<tr>
<td>Final Height (mm)</td>
<td>226</td>
<td>157</td>
<td>166</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Control</th>
<th>“A” #4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Choice Time (80%H, seconds)</td>
<td>5.8</td>
<td>6.7</td>
</tr>
<tr>
<td>Rise Time (98% H, seconds)</td>
<td>6.7</td>
<td>7.9</td>
</tr>
<tr>
<td>Maximum Height (mm)</td>
<td>231</td>
<td>222</td>
</tr>
<tr>
<td>Final Height (mm)</td>
<td>226</td>
<td>219</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Components</th>
<th>#5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyether Polyol</td>
<td>30.94</td>
</tr>
<tr>
<td>Emulsifier (same as above)</td>
<td>9.88</td>
</tr>
</tbody>
</table>
EXAMPLE 5

Foam Rate of Rise Comparison of Catalyst Combination "A" Polycat®-15/Dabco®-T With and Without TMG

In this example catalyst combination "A" was used at 9.0 parts and compared with another combination that contain 8.5 parts of "A" together with 0.5 parts TMG. The formulations and kinetic data are shown below.

<table>
<thead>
<tr>
<th>Components</th>
<th>Control</th>
<th>&quot;B&quot;</th>
<th>#5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyether Polyol</td>
<td>30.94</td>
<td>30.94</td>
<td></td>
</tr>
<tr>
<td>Emulsifier (same as above)</td>
<td>9.88</td>
<td>9.88</td>
<td></td>
</tr>
<tr>
<td>Flame Retardant (TCPP)</td>
<td>23.74</td>
<td>23.74</td>
<td></td>
</tr>
<tr>
<td>Surfactant (same as above)</td>
<td>1.05</td>
<td>1.05</td>
<td></td>
</tr>
<tr>
<td>Cell Opener (same as above)</td>
<td>0.05</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>TMG (Tetramethyguanidine)</td>
<td>0.00</td>
<td>0.50</td>
<td></td>
</tr>
<tr>
<td>Catalyst &quot;A&quot;</td>
<td>9.00</td>
<td>8.50</td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>18.05</td>
<td>18.05</td>
<td></td>
</tr>
<tr>
<td>MDI</td>
<td>91.23</td>
<td>91.23</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Control (#1)</th>
<th>Comp. (#6)</th>
<th>#7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Choice Time (80%H, seconds)</td>
<td>5.8</td>
<td>6.1</td>
<td>5.5</td>
</tr>
<tr>
<td>Rise Time (98% H, seconds)</td>
<td>6.7</td>
<td>7.2</td>
<td>6.7</td>
</tr>
<tr>
<td>Maximum Height (mm)</td>
<td>231</td>
<td>216</td>
<td>204</td>
</tr>
<tr>
<td>Final Height (mm)</td>
<td>226</td>
<td>211</td>
<td>201</td>
</tr>
</tbody>
</table>

[0059] In both cases 6 and 7 the same total amount of catalyst was used (9.0 parts) but in # 6 all 9.0 parts are catalyst
"A" while in # 7 a smaller amount of "A" was used (8.5 parts) and the remaining 0.5 parts were completed by the addition of TMG to give also 9.0 parts of total catalyst added. The result clearly indicates that the catalyst system containing a small amount of TMG (5.5 % of the total catalyst blend) was faster than "A".

EXAMPLE 6

Foam Rate of Rise Comparison Between BMDAEE/DMAEE Control, Non-Emissive Catalyst Combination Polycat®-15/Dabco®-T and Non-Emissive Catalyst Combination "C" Containing TMG (Tetramethylguanidine)

In this example, 8.5 parts of a catalyst combination "C" having the following components: a) bis-(dimethylaminopropyl) amine (82.5 %; Polycat®-15); b) 2-[N-(dimethylaminoethoxyethyl)-N-methylamino] ethanol (12.5 %); c) Tetramethylguanidine (5.0 %) were compared with the standard BDMAEE/DMAEE described in example 1 (foam #1) and with the non-emissive catalyst combination described in example 3 (foam #4). The formulation for foam # 8 is shown in the following table:

<table>
<thead>
<tr>
<th>Components</th>
<th>#8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyether Polyl</td>
<td>30.94</td>
</tr>
<tr>
<td>Emulsifier (same as above)</td>
<td>9.88</td>
</tr>
<tr>
<td>Flame Retardant (TCPP)</td>
<td>23.74</td>
</tr>
<tr>
<td>Surfactant (same as above)</td>
<td>1.05</td>
</tr>
<tr>
<td>Cell Opener (same as above)</td>
<td>0.05</td>
</tr>
<tr>
<td>(Bis(dimethylaminopropyl)amine) (Polycat®-15)</td>
<td>7.01</td>
</tr>
<tr>
<td>2-[N-(dimethylaminoethoxyethyl)-N-methylamino] ethanol</td>
<td>1.06</td>
</tr>
<tr>
<td>TMG</td>
<td>0.42</td>
</tr>
<tr>
<td>Water</td>
<td>18.05</td>
</tr>
<tr>
<td>MDI</td>
<td>91.23</td>
</tr>
</tbody>
</table>

Catalyst combination "C" provides provides rate of rise profile that not only replicates the choice time and rise time of the control but also the maximum height and final height. It is very surprising that when adding a small amount of TMG (5.0 % of total catalyst loading) a substantial increase in the reaction rate occur so that the kinetic of the control could be reproduced. Such result was not possible in the absence of TMG as already demonstrated in the previous examples.

EXAMPLE 7

Foam Rate of Rise Comparison Between BMDAEE/DMAEE Control, Non-Emissive Catalyst Combination Polycat®-15/Dabco®-T and Non-Emissive Catalyst Combination "D" Containing TMG (Tetramethylguanidine)

In this example, 8.5 parts of a catalyst combination "D" having the following components: a) bis-(dimethylaminopropyl) amine (82.5 %; Polycat®-15); b) N,N,N-trimethyl-N-3-aminopropyl-bis(aminoethyl) ether (12.5 %; Dabco®NE300); c) Tetramethylguanidine (5.0 %) were compared with the standard BDMAEE/DMAEE described in example 1 (foam #1) and with the non-emissive catalyst combination described in example 3 (foam #4). The formulation for foam # 9 is shown in the following table:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Control #1</th>
<th>Comp. #4</th>
<th>Catalyst &quot;C&quot; #8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Choice Time (mm, 80%H, seconds)</td>
<td>5.8</td>
<td>6.7</td>
<td>5.7</td>
</tr>
<tr>
<td>Rise Time (seconds, 98% H)</td>
<td>6.7</td>
<td>7.9</td>
<td>6.8</td>
</tr>
<tr>
<td>Maximum Height (mm)</td>
<td>231</td>
<td>222</td>
<td>239</td>
</tr>
<tr>
<td>Final Height (mm)</td>
<td>226</td>
<td>219</td>
<td>234</td>
</tr>
</tbody>
</table>
Catalyst combination “D” provides rate of rise profile that not only replicates the choice time and rise time of the control but also the maximum height and final height. As shown in previous examples, adding a small amount of TMG (5.0 % of total catalyst loading) increased the reaction rate so that the rate of rise kinetic matched the standard. Such result was not possible in the absence of TMG as already demonstrated in the previous examples. Catalyst combination “D” is analogous to “C” but in “D” the blowing catalyst N,N,N’-trimethyl-N’-3-aminopropyl-bis(amoineethyl) ether having a primary amine group was used. This catalyst is structurally related to BDMAEE because it also has the N-C2-O-C2-N backbone needed for water activation. Thus both combinations “C” and “D” having 5.0 % of TMG (based on total catalyst loading) are very effective and most comparable to the emissive standard control. A similar case was also found for catalyst combination “E” which also contains 5.0 % TMG.

<table>
<thead>
<tr>
<th>Components</th>
<th>#9</th>
<th>#10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyether Polyol</td>
<td>30.94</td>
<td>30.94</td>
</tr>
<tr>
<td>Emulsifier (same as above)</td>
<td>9.88</td>
<td>9.88</td>
</tr>
<tr>
<td>Flame Retardant (TCPP)</td>
<td>23.74</td>
<td>23.74</td>
</tr>
<tr>
<td>Surfactant (same as above)</td>
<td>1.05</td>
<td>1.05</td>
</tr>
<tr>
<td>Cell Opener (same as above)</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>(Polycat®-15)</td>
<td>7.01</td>
<td>7.01</td>
</tr>
<tr>
<td>N,N,N’-trimethyl-N’-3-aminopropyl-bis(amoineethyl) ether</td>
<td>1.06</td>
<td>0.53</td>
</tr>
<tr>
<td>2-[N-(dimethylaminoethoxyethyl)-N-methylamino] ethanol (Dabco®T)</td>
<td>0.00</td>
<td>0.53</td>
</tr>
<tr>
<td>TMG</td>
<td>0.42</td>
<td>0.42</td>
</tr>
<tr>
<td>Water</td>
<td>18.05</td>
<td>18.05</td>
</tr>
<tr>
<td>MDI</td>
<td>91.23</td>
<td>91.23</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Control #1</th>
<th>Comp. #4</th>
<th>Catalyst “C” #8</th>
<th>Catalyst “D” #9</th>
<th>Catalyst “E” #10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Choice Time (mm, 80%H, seconds)</td>
<td>5.8</td>
<td>6.7</td>
<td>5.7</td>
<td>5.4</td>
<td>5.4</td>
</tr>
<tr>
<td>Rise Time (seconds, 98% H, seconds)</td>
<td>6.7</td>
<td>7.9</td>
<td>6.8</td>
<td>6.4</td>
<td>6.4</td>
</tr>
<tr>
<td>Maximum Height (mm)</td>
<td>231</td>
<td>222</td>
<td>239</td>
<td>227</td>
<td>224</td>
</tr>
<tr>
<td>Final Height (mm)</td>
<td>226</td>
<td>219</td>
<td>234</td>
<td>222</td>
<td>220</td>
</tr>
</tbody>
</table>

Originally filed claims:

1. A catalyst composition for catalyzing the formation of a polyurethane foam comprising:
   at least one non-emissive catalyst and a tetraalkyl guanidine of the following formula

![Chemical Structure](image)

wherein R1, R2, R3 and R4 are independently C1-C10 alkyl groups and branched or un-branched isomers thereof.
2. The catalyst composition of Clause 1 consisting essentially of at least one non-emissive catalyst and a tetraalkyl guanidine of the following formula

\[
\begin{array}{c}
\text{N} \\
R_1 \quad \text{N} \\
\text{R}_2 \quad \text{N} \\
\text{R}_3 \quad \text{R}_4
\end{array}
\]

wherein R1, R2, R3 and R4 are independently C1-C10 alkyl groups and linear or branched isomers thereof.

3. The catalyst composition of Clause 1 or 2, wherein the polyurethane foam is formed in the presence of a blowing agent composition comprising water.

4. The catalyst composition of Clause 1 or 2, wherein the polyurethane foam is formed in the presence of a blowing agent composition consisting of water.

5. The catalyst composition of Clause 1 or 2, wherein the tetraalkyl guanidine comprises tetramethyl guanidine.

6. The catalyst composition of Clause 1 or 2, wherein the amount of the tetraalkyl guanidine in the catalyst composition is sufficient to achieve a Choice Time as measured by a sonar detector of 5.8 seconds or shorter.

7. The catalyst composition of Clause 1 or 2, wherein the amount of the tetraalkyl guanidine comprises about 40% or less by weight of the total catalyst composition.

8. The catalyst composition of Clause 1 or 2, wherein the amount of the tetraalkyl guanidine comprises about 30% or less by weight of the total catalyst composition.

9. The catalyst composition of Clause 1 or 2, wherein the amount of the tetraalkyl guanidine comprises about 5% or less by weight of the total catalyst composition.

10. The catalyst composition of Clause 1 or 2, wherein the non-emissive catalyst comprises at least one member selected from the group consisting of bis-(N,N-dimethylaminopropyl)-amine, 6-dimethylamino-1-hexanol, N,N,N'-trimethylaminoethyl-ethanolamine, (N,N-dimethylaminopropyl-N'-methyl-N'- (2-hydroxyethyl) amine, dimethyl ethanolamine, N,N-bis(3-dimethylamino-propyl)-N-(2-hydroxypropyl) amine, N,N,N'-trimethyl-N'-bis(2-hydroxypropyl)-1,3-propylenediamine, 2-(2-dimethylaminoethoxy)ethanol, dimethylaminopropylurea, bis(dimethylaminopropyl)urea, 2-[N-(dimethylaminoethoxyethyl)-N-methylamino] ethanol, N,N,N'-trimethyl-N'-3-aminopropyl-bis(aminooethyl) ether, dimethylaminopropylamine, N-methyl-N-2-hydroxypropyl-piperazine, bis(dimethylamino)-2-propanol, N-(3-aminopropyl)imidazole, N-(2-hydroxypropyl)imidazol and any combination thereof.

11. The catalyst composition of Clause 1 or 2, wherein the at least one non-emissive catalyst comprises bis(dimethylaminopropyl) amine and N-(dimethylaminooethyl)-N-(2-hydroxyethyl)-N-methylamine.

12. The catalyst composition of Clause 1 or 2, wherein the at least one non-emissive catalyst comprises bis(dimethylaminopropyl) amine and 2-[N-(dimethylaminoethoxyethyl)-N-methylamino] ethanol.

13. The catalyst composition of Clause 1 or 2, wherein the at least one non-emissive catalysts comprise bis(dimethylaminopropyl) amine and N,N,N'-trimethyl-N'-3-aminopropyl-bis(aminooethyl) ether.

14. The catalyst composition of Clause 1 or 2, wherein the polyurethane foam formed has a density of about 6 to about 16 Kg/m³

15. A catalyst composition for catalyzing the formation of a polyurethane foam comprising about 70% or more by weight of N,N,N'-trimethyl-N'-3-aminopropyl-bis(aminooethyl) ether and about 30% or less by
weight of tetramethyl guanidine.

16. A method for preparing a water blown, low density, rigid polyurethane foam which comprises contacting at least one polyisocyanate with at least one polyol, at an Isocyanate Index of 20 to 100, in the presence of an effective amount of a blowing agent composition comprising at least 75 wt% water and an effective amount of a catalyst composition according to Clause 1, the rigid polyurethane foam having a density of about 6 to about 16 Kg/m³.

17. The method of Clause 16, wherein the Isocyanate Index is 20 to 50.

18. The method of Clause 16, wherein the tetraalkyl guanidine comprises tetramethyl guanidine.

19. The method of Clause 16, wherein the amount of the tetraalkyl guanidine comprises about 40% or less by weight of the total catalyst composition.

20. The method of Clause 16, wherein the amount of the tetraalkyl guanidine comprises about 30% or less by weight of the total catalyst composition.

21. The method of Clause 16, wherein the amount of the tetraalkyl guanidine comprises about 5% or less by weight of the total catalyst composition.

22. A polyurethane foam formulation comprising at least one polyol, at least an isocyanate, an effective amount of a blowing agent composition and an effective amount of a catalyst composition according to Clause 1.

23. The polyurethane foam formulation of Clause 22, further comprises at least one member selected from a group consisting of a surfactant, an emulsifier, a flame retardant, a crosslinker, a cell stabilizer and a combination thereof.

24. The polyurethane foam formulation of Clause 23, wherein the blowing agent composition comprises water.

25. The polyurethane foam formulation of Clause 23, wherein the tetraalkyl guanidine comprises tetramethyl guanidine.

26. The polyurethane foam formulation of Clause 23, wherein the amount of the tetraalkyl guanidine comprises about 40% or less by weight of the total catalyst composition.

27. The polyurethane foam formulation of Clause 23, wherein the amount of the tetraalkyl guanidine comprises about 30% or less by weight of the total catalyst composition.

28. The polyurethane foam formulation of Clause 23, wherein the amount of the tetraalkyl guanidine comprises about 5% or less by weight of the total catalyst composition.

29. The polyurethane foam formulation of Clause 22, wherein the polyurethane foam having a density of about 6 to about 16 Kg/m³.

30. The polyurethane foam formulation of Clause 29, wherein the polyurethane foam having a density of about 8 Kg/m³.

Claims

1. A catalyst composition for catalyzing the formation of a polyurethane foam comprising:

   at least one non-emissive catalyst and a tetraalkyl guanidine of the following formula
wherein R1, R2, R3 and R4 are independently C1-C10 alkyl groups and branched or un-branched isomers thereof, wherein the at least one non-emissive catalyst comprises bis(dimethylaminopropyl) amine and a compound selected from the group of N-(dimethylaminooethyl)-N-(2-hydroxyethyl)-N-methylamine, 2-[N-(dimethylaminoethoxyethyl)-N-methylamino] ethanol, and N,N,N'-trimethyl-N'-3-aminopropyl-bis(aminoethyl) ether.

2. The catalyst composition of Claim 1 consisting essentially of at least one non-emissive catalyst and a tetraalkyl guanidine of the following formula

wherein R1, R2, R3 and R4 are independently C1-C10 alkyl groups and linear or branched isomers thereof.

3. The catalyst composition of Claim 1 or 2, wherein the polyurethane foam is formed in the presence of a blowing agent composition comprising water.

4. The catalyst composition of Claim 1 or 2, wherein the tetraalkyl guanidine comprises tetramethyl guanidine.

5. The catalyst composition of Claim 1 or 2, wherein the amount of the tetraalkyl guanidine in the catalyst composition is sufficient to achieve a Choice Time as measured by a sonar detector of 5.8 seconds or shorter.

6. The catalyst composition of Claim 1 or 2, wherein the amount of the tetraalkyl guanidine comprises 40% or less by weight of the total catalyst composition.

7. The catalyst composition of Claim 1 or 2, wherein the non-emissive catalyst comprises at least one member selected from the group consisting of bis-(N,N-dimethylaminopropyl)-amine, 6-dimethylamino-1-hexanol, N,N,N'-trimethylaminoethyl-ethanolamine, (N,N-dimethylaminopropyl-N'-methyl-2-hydroxyethyl)amine, dimethylethanolamine, N,N-bis(3-dimethylamino-propyl)-N-(2-hydroxypropyl) amine, N,N-dimethyl-N',N'-bis(2-hydroxypropyl)-1,3-propylene diamine, 2-(2-dimethylaminoethoxy)ethanol, dimethylenepropylurea, bis(dimethylenepropyl)urea, 2-[N-(dimethylaminoethoxyethyl)-N-methylamino] ethanol, N,N,N'-trimethyl-N'-3-aminopropyl-bis(aminoethyl) ether, dimethylaminopropylamine, N-methyl-N-2-hydroxypropyl-piperazine, bis(dimethylamino)-2-propanol, N-(3-aminopropyl)imidazole, N-(2-hydroxypropyl)imidazol and any combination thereof.

8. The catalyst composition of Claim 1 or 2, wherein the polyurethane foam formed has a density of 6 to 16 Kg/m³.

9. A catalyst composition for catalyzing the formation of a polyurethane foam comprising 70% or more by weight of N,N,N'-trimethyl-N'-3-aminopropyl-bis(aminoethyl) ether and 30% or less by weight of tetramethyl guanidine.

10. A method for preparing a water blown, low density, rigid polyurethane foam which comprises contacting at least one polyisocyanate with at least one polyol, at an Isocyanate Index of 20 to 100, in the presence of an effective amount of a blowing agent composition comprising at least 75 wt% water and an effective amount of a catalyst composition according to any of claims 1 to 9, the rigid polyurethane foam having a density of 6 to 16 Kg/m³.
11. The method of Claim 10, wherein the Isocyanate Index is 20 to 50.

12. The method of Claim 10, wherein the tetraalkyl guanidine comprises tetramethyl guanidine.

13. The method of Claim 10, wherein the amount of the tetraalkyl guanidine comprises 40% or less by weight of the total catalyst composition.

14. A polyurethane foam formulation comprising at least one polyol, at least an isocyanate, an effective amount of a blowing agent composition and an effective amount of a catalyst composition according to any of claims 1 to 9.

15. The polyurethane foam formulation of Claim 14, further comprises at least one member selected from a group consisting of a surfactant, an emulsifier, a flame retardant, a crosslinker, a cell stabilizer and a combination thereof.

**Patentansprüche**

1. Katalysatorzusammensetzung zum Katalysieren der Bildung eines Polyurethanschaums, umfassend:

   mindestens einen emissionsfreien Katalysator und ein Tetraalkylguanidin mit der folgenden Formel:

   ![Chemical Structure](image)

   wobei R₁, R₂, R₃ und R₄ unabhängig C₁⁻C₁₀-Alkylgruppen und verzweigte oder unverzweigte Isomere davon sind,

   wobei der mindestens eine emissionsfreie Katalysator Bis(dimethylaminopropyl)amin und eine Verbindung ausgewählt aus N-(Dimethylaminoethyl)-N-(2-hydroxyethyl)-N-methylamin, 2-[N-(Dimethylaminoethoxyethyl)-N-methylamino]ethanol und N,N,N'-Trimethyl-N'-3-aminopropyl-bis(aminoethyl)ether umfasst.

2. Katalysatorzusammensetzung nach Anspruch 1, die im Wesentlichen aus mindestens einem emissionsfreien Katalysator und einem Tetraalkylguanidin mit der folgenden Formel besteht:

   ![Chemical Structure](image)

   wobei R₁, R₂, R₃ und R₄ unabhängig C₁⁻C₁₀-Alkylgruppen und lineare oder verzweigte Isomere davon sind.

3. Katalysatorzusammensetzung nach Anspruch 1 oder 2, wobei der Polyurethanschaum in Gegenwart einer Treibmittelzusammensetzung gebildet wird, die Wasser umfasst.

4. Katalysatorzusammensetzung nach Anspruch 1 oder 2, wobei das Tetraalkylguanidin Tetramethylguanidin umfasst.

5. Katalysatorzusammensetzung nach Anspruch 1 oder 2, wobei die Menge des Tetraalkylguanidins in der Katalysatorzusammensetzung ausreicht, um eine Wahlzeit, gemessen mittels Sonardetektor, von 5,8 Sekunden oder kürzer zu erreichen.
6. Katalysatorzusammensetzung nach Anspruch 1 oder 2, wobei die Menge des Tetraalkylguanidins 40 % oder weniger von dem Gewicht der gesamten Katalysatorzusammensetzung umfasst.

7. Katalysatorzusammensetzung nach Anspruch 1 oder 2, wobei der emissionsfreie Katalysator mindestens ein Mitglied ausgewählt aus der Gruppe bestehend aus Bis-(N,N-dimethylaminopropyl)-amin, 6-Dimethylamino-1-hexanol, N,N,N'-Trimethylaminoethylethanolamin, (N,N-Dimethylaminopropyl)-N-methyl-N-(2-hydroxyethyl)-amin, Dimethylethanolamin, N,N-Bis(3-dimethylaminopropyl)-N-(2-hydroxypropyl)-amin, N,N-Dimethyl-N',N'-bis(2-hydroxypropyl)-1,3-propyldiamin, 2-(2-Dimethylaminooethoxy)ethanol, Dimethylenimipropylharnstoff, Bis(dimethylaminopropyl)harnstoff, 2-[N-Dimethylaminoethoxyethyl-N-methylamin]-ethanol, N,N,N'-Trimethyl-N'-3-amino-propyl-bis(aminoethyl)-ether, Dimethylenimipropylamin, N-Methyl-N-2-hydroxypropylpiperazin, Bis(dimethylamino)-2-propanol, N-(3-Aminopropyl)imidazol, N-(2-Hydroxypropyl)imidazol und jedwede Kombination davon umfasst.

8. Katalysatorzusammensetzung nach Anspruch 1 oder 2, wobei der gebildete Polyurethanschaum eine Dichte von 6 bis 16 Kg/m³ aufweist.


10. Verfahren zum Herstellen eines wassergetriebenen steifen Polyurethanschaums mit niedriger Dichte, umfassend Kontaktieren von mindestens einem Polyisocyanat mit mindestens einem Polyol mit einem Isocyanatindex von 20 bis 100 in Gegenwart einer effektiven Menge einer Treibmittelzusammensetzung, umfassend mindestens 75 Gew. % Wasser und eine effektive Menge einer Katalysatorzusammensetzung gemäß einem der Ansprüche 1 bis 9, wobei der steife Polyurethanschaum eine Dichte von 6 bis 16 Kg/m³ aufweist.

11. Verfahren nach Anspruch 10, wobei der Isocyanatindex 20 bis 50 ist.

12. Verfahren nach Anspruch 10, wobei das Tetraalkylguanidin Tetramethylguanidin umfasst.

13. Verfahren nach Anspruch 10, wobei die Menge des Tetraalkylguanidins 40 % oder weniger von dem Gewicht der gesamten Katalysatorzusammensetzung umfasst.


Revendications

1. Composition de catalyseur destinée à catalyser la formation d’une mousse de polyuréthane, comprenant :

au moins un catalyseur non émissif et une tétraalkylguanidine ayant la formule suivante :

\[
\begin{align*}
\text{N} & \quad \text{R}_1 \\
\text{R}_2 & \quad \text{N} \\
\text{R}_3 & \quad \text{R}_4 \\
\end{align*}
\]

daussi que R1, R2, R3 et R4 sont indépendamment des groupes alkyle C1-C10 et des isomères ramifiés ou non ramifiés de ceux-ci,
dans laquelle ledit au moins un catalyseur non émissif comprend de la bis(diméthylaminopropyl)amine et un composé sélectionné dans le groupe constitué de la N-(diméthylaminoéthyl)-N-(2-hydroxyéthyl)-N-méthylamine, du 2[N-(diméthylaminoéthoxyéthyl)-N-méthylamino]éthanol, et du N,N,N'-triméthyl-N'-3-aminopropyl-bis(aminéthyle)éther.

2. Composition de catalyseur selon la revendication 1, consistant essentiellement en au moins un catalyseur non émissif et une tétraalkylguanidine ayant la formule suivante :

![Diagramme de la formule de la tétraalkylguanidine]

dans laquelle R1, R2, R3 et R4 sont indépendamment des groupes alkyle C1-C10 et des isomères linéaires ou ramifiés de ceux-ci.

3. Composition de catalyseur selon la revendication 1 ou 2, dans laquelle la mousse de polyuréthane est formée en présence d’une composition d’agent gonflant comprenant de l’eau.

4. Composition de catalyseur selon la revendication 1 ou 2, dans laquelle la tétraalkylguanidine comprend la tétraméthylguanidine.

5. Composition de catalyseur selon la revendication 1 ou 2, dans laquelle la quantité de la tétraalkylguanidine dans la composition de catalyseur est suffisante pour produire un Choice Time, tel que mesuré par un détecteur sonar, de 5,8 secondes ou plus court.

6. Composition de catalyseur selon la revendication 1 ou 2, dans laquelle la quantité de la tétraalkylguanidine représente 40 % en poids ou moins de la composition de catalyseur totale.

7. Composition de catalyseur selon la revendication 1 ou 2, dans laquelle le catalyseur non émissif comprend au moins un élément sélectionné dans le groupe constitué de la bis-(N,N-diméthylaminopropyl)-amine, du 6-diméthylaminol-1-hexanol, de la N,N,N'-triméthylaminoéthyl-éthanolamine, de la (N,N-diméthylaminopropyl-N'-méthyl-N'-2-hydroxyéthyl)amine, de la diméthyléthanolamine, de la N,N-bis(3-diméthylamino-propyl)-N-(2-hydroxypropyl)amine, de la N,N-diméthyl-N',N'-bis(2-hydroxypropyl)-1,3-propénynediamine, du 2-[N-(diméthylaminoéthoxyéthyl)-éthanol, de la diméthylaminopropylurée, de la bis(diméthylaminopropyl)urée, du 2-[N-(diméthylaminoéthoxyéthyl)-N-méthylamino]éthanol, du N,N,N'-triméthyl-N'-3-aminopropyl-bis(aminéthyle)éther, de la diméthylaminopropylamine, de la N-méthyl-N-2-hydroxypropyl-pipérazine, du bis(diméthylamino)-2-propanol, du N(3-aminopropyl)imidazole, du N-(2-hydroxypropyl)imidazole, et de n’importe quelle combinaison de ceux-ci.

8. Composition de catalyseur selon la revendication 1 ou 2, dans laquelle la mousse de polyuréthane formée a une densité de 6 à 16 kg/m³.

9. Composition de catalyseur destinée à catalyser la formation d’une mousse de polyuréthane, comprenant :

70 % en poids ou plus de N,N,N'-triméthyl-N'-3-aminopropyl-bis(aminéthyle)éther et 30 % en poids ou moins de tétraméthylguanidine.

10. Procédé de préparation d’une mousse de polyuréthane rigide, soufflée à l’eau, de basse densité, qui comprend la mise en contact d’au moins un polyisocyanate avec au moins un polyol, selon un indice d’isocyanate de 20 à 100, en présence d’une quantité efficace d’une composition d’agent gonflant comprenant au moins 75 % en poids d’eau et d’une quantité efficace d’une composition de catalyseur selon l’une quelconque des revendications 1 à 9, la mousse de polyuréthane rigide ayant une densité de 6 à 16 kg/m³.

11. Procédé selon la revendication 10, dans lequel l’indice d’isocyanate est de 20 à 50.
12. Procédé selon la revendication 10, dans lequel la tétraalkylguanidine comprend la tétraméthylguanidine.

13. Procédé selon la revendication 10, dans lequel la quantité de la tétraalkylguanidine représente 40 % en poids ou moins de la composition de catalyseur totale.

14. Formulation de mousse de polyuréthane comprenant :

   au moins un polyol, au moins un isocyanate, une quantité efficace d’une composition d’agent gonflant, et une quantité efficace d’une composition de catalyseur selon l’une quelconque des revendications 1 à 9.

15. Formulation de mousse de polyuréthane selon la revendication 14, comprenant en outre au moins un élément sélectionné dans un groupe constitué d’un tensioactif, d’un émulsifiant, d’un agent ignifuge, d’un agent de réticulation, d’un stabilisateur d’alvéoles, et d’une combinaison de ceux-ci.
REFERENCES CITED IN THE DESCRIPTION

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