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(54) **Title**: IMPROVED STABILITY OF POLYURETHANE POLYOL BLENDS CONTAINING HALOGENATED OLEFIN BLOWING AGENT

(57) **Abstract**: A polyol pre-mix composition includes a blowing agent having a halogenated hydroolefin, a polyol, a surfactant, a catalyst composition, and a metal salt. The metal salt may be, for example, a carboxylate, acetylacetonate, alcoholate of a metal selected from the group consisting of Zn, Co, Ca, and Mg. The metal salt may be, for example, a carboxylate and/or alcoholate of a C1-C21 straight chain or branched aliphatic monocarboxylic acid or monoalcohol, such as magnesium formate, zinc octoate, calcium octoate, cobalt octoate, and magnesium octoate, and mixtures thereof. The metal acetylacetonate may be, for example, zinc acetylacetonate, cobalt acetylacetonate, magnesium acetylacetonate, or calcium acetylacetonate. A two-part system for producing a thermosetting foam blend includes (a) a polyisocyanate and, optionally, one or more isocyanate compatible raw materials; and (b) the polyol pre-mix composition. A method for producing a thermosetting foam blend includes combining: (a) a polyisocyanate; and (b) the polyol pre-mix composition.

IMPROVED STABILITY OF POLYURETHANE POLYOL BLENDS CONTAINING HALOGENATED OLEFIN BLOWING AGENT

FIELD OF THE INVENTION

The present invention relates to a method for stabilizing thermosetting foam blends that include halogenated olefinic blowing agent, such as hydrochlorofluoroolefin (HCFO) HCFO-1233zd. More particularly, the present invention relates to a method for stabilizing thermosetting foam blends using a polyol pre-mix composition which includes one or more metal salts. The present invention further relates to the stable pre-blend formulations and resulting polyurethane or polyisocyanurate foams.

BACKGROUND OF THE RELATED ART

The Montreal Protocol for the protection of the ozone layer mandated the phase-out of the use of chlorofluorocarbons (CFCs). Materials more "friendly" to the ozone layer, such as hydrofluorocarbons (HFCs), e.g., HFC-134a, replaced chlorofluorocarbons. The latter compounds have proven to be green house gases, causing global warming, and were regulated by the Kyoto Protocol on Climate Change. The emerging replacement materials, hydrofluoropropenes, were shown to be environmentally acceptable, i.e., they have zero ozone depletion potential (ODP) and acceptable low global warming potential (GWP).

Currently used blowing agents for thermoset foams include HFC-134a, HFC-245fa, HFC-365mfc, which have relatively high global warming potential, and hydrocarbons such as pentane isomers, which are flammable and have low energy efficiency. Therefore, new alternative blowing agents are being sought. Halogenated hydroolefinic materials such as hydrofluoropropenes and/or hydrochlorofluoropropenes have generated interest as replacements for HFCs. The inherent chemical instability of these materials in the lower atmosphere provides for a low global warming potential and zero or near zero ozone depletion properties desired.

It is convenient in many applications to provide the components for polyurethane or polyisocyanurate foams in pre-blended formulations. Most typically,

the foam formulation is pre-blended into two components. The polyisocyanate and optional isocyanate compatible raw materials comprise the first component, commonly referred to as the "A-" side component. A polyol or mixture of polyols, surfactant, catalyst, blowing agent, and other isocyanate reactive and non-reactive components comprise the second component, commonly referred to as the "B-" side component. Accordingly, polyurethane or polyisocyanurate foams are readily prepared by bringing together the A- and B- side components either by hand mix for small preparations and, preferably, machine mix techniques to form blocks, slabs, laminates, pour-in-place panels and other items, spray applied foams, froths, and the like.

Two-component systems, however, have been found to have reduced shelf-life of the B-side composition, especially those systems which use certain hydrohaloolefins such as HFO-1234ze and HCFO-1233zd. Normally when a foam is produced by bringing together the A and B side components, a good foam is obtained. However, if the polyol pre-mix composition is aged prior to treatment with the polyisocyanate, the foams are of lower quality and may even collapse during the formation of the foam. The poor foam structure is attributed to the reaction of certain catalysts with certain hydrohaloolefins, including HFO-1234ze and HCFO-1233zd, which results in the partial decomposition of the blowing agent and, subsequently, the undesirable modification of the polymeric silicone surfactants.

One way to overcome this problem, for example, is by separating the blowing agent, surfactant, and catalyst, and introducing them using a separate stream from the "A-" or "B-" side components. However, a preferred solution would not require such reformulation or process change. A more favorable method may be to utilize a catalyst that has a lower reactivity towards certain blowing agents. The commonly used catalysts for polyurethane chemistry can be classified into two broad categories: amine compounds and organometallic complexes. Amine catalysts are generally selected based on whether they drive: the gel catalysis (or polymerization) reaction, in which polyfunctional isocyanates react with polyols to form polyurethane, or the blow catalysis (or gas-producing) reaction, in which the isocyanate reacts with water to form polyurea and carbon dioxide. Amine catalysts can also drive the isocyanate trimerization reaction. Since some amine catalysts will drive all three reactions to some extent, they are often selected based on how much they favor one reaction over another. As certain amine catalysts are now known to have a detrimental effect on the

halogenated olefinic blowing agents, a stable polyol pre-mix composition is desired which will reduce or eliminate such detrimental interactions. Additionally, a method for stabilizing thermosetting foam blends, the resulting stable pre-mix blend formulations, and the environmentally-friendly polyurethane or polyisocyanurate foams having good foam structure remain highly desirable.

BRIEF SUMMARY OF THE INVENTION

It has now been discovered that metal salts can function to stabilize polyol pre-mix compositions which contain catalysts and blowing agents. Specifically, it has now been discovered that metal salts may be favorably used to stabilize a polyol pre-mix B-side containing a halogenated hydroolefin blowing agent. The stabilization method was found to prolong the shelf life of the pre-mix and enhance the foam characteristics of the foam obtained by combining the polyol pre-mix composition with a polyisocyanate.

Accordingly, the polyol pre-mix compositions containing metal salts are a favorable replacement for traditional polyol pre-mixes which were found to have negative interactions between the catalyst, such as an amine catalyst, and the halogenated hydroolefin. Without being held to any theory, the metal salts are thought to protect the surfactant from a Nucleophilic attack by the catalyst, such as an amine catalyst, and may also act as acid (e.g., hydrofluoric acid) scavengers. The metal salts can be used as a stabilizing component of a polyol pre-mix blend, in the process for stabilizing thermosetting foam blends, and in the resultant polyurethane or polyisocyanurate foams. The method of the present invention was found to surprisingly stabilize the polyol pre-mix composition, thereby providing longer shelf life. That is, polyol pre-mix compositions in accordance with the present invention are capable of being stored for long periods of time with little or no detrimental effect on their characteristics and properties. Foams produced by reacting the polyol pre-mix compositions of the present invention with an A side component containing polyisocyanate were found to have enhanced foam characteristics and may be employed to meet the demands of low or zero ozone depletion potential, lower global warming potential, low VOC content, and low toxicity, thereby making them environmentally-friendly.

In one embodiment, the present invention provides a polyol pre-mix

composition which comprises a blowing agent, a polyol, a surfactant, a catalyst composition, and a metal salt. The catalyst composition may comprise an amine catalyst or non-amine catalyst. The blowing agent may comprise a halogenated hydroolefin and, optionally, hydrofluorocarbons (HFCs), hydrofluoroethers (HFEs), hydrocarbons, alcohols, aldehydes, ketones, ethers/diethers, esters, or CO_2 generating materials, or combinations thereof. The surfactant may be a silicone or non-silicone surfactant. In another embodiment the present invention provides a two-part system for producing a thermosetting foam blend, wherein the system comprises: (a) as a first part, a polyisocyanate and, optionally, one or more isocyanate compatible raw materials; and (b) as a second part, a polyol pre-mix composition which comprises a blowing agent, a polyol, a surfactant, a catalyst composition, and a metal salt. The catalyst composition may comprise an amine catalyst or non-amine catalyst.

In a further embodiment, the present invention is a method for producing a thermosetting foam blend which comprises combining: (a) a polyisocyanate and, optionally, one or more isocyanate compatible raw materials; and (b) a polyol pre-mix composition which comprises a blowing agent, a polyol, a surfactant, a catalyst composition, and a metal salt. The catalyst composition may comprise an amine catalyst or non-amine catalyst. In yet another embodiment, the present invention provides a mixture suitable for providing a polyurethane or polyisocyanurate foam having uniform cell structure with little or no foam collapse, wherein the mixture comprises: (a) a polyisocyanate and, optionally, one or more isocyanate compatible raw materials; and (b) a polyol pre-mix composition which comprises a blowing agent, a polyol, a surfactant, a catalyst composition, and a metal salt. The catalyst composition may comprise an amine catalyst or non-amine catalyst. Accordingly, polyurethane or polyisocyanurate foams are readily prepared by bringing together the A- and B-side components either by hand mix for small preparations and, preferably, machine mix techniques to form blocks, slabs, laminates, pour-in-place panels and other items, spray applied foams, froths, and the like.

It has unexpectedly been discovered that metal salts function to stabilize polyol pre-mix compositions by offsetting the detrimental reactivity between traditional catalysts and hydrohaloolefins. The use of one or more metal salts in a polyol pre-mix blend composition surprisingly produces a thermoset blend composition that has improved shelf-life stability. The metal salts may be metal carboxylates, metal acetylacetonates, metal alcoholates, for example, alkali earth

carboxylates, alkali earth acetylacetonates and alcoholates, alkali carboxylates, alkali acetylacetonates and alcoholates, and carboxylates, acetylacetonates and alcoholates of zinc (Zn), cobalt (Co), tin (Sn), cerium (Ce), lanthanum (La), aluminum (Al), vanadium (V), manganese (Mn), copper (Cu), nickel (Ni), iron (Fe), titanium (Ti), zirconium (Zr), chromium (Cr), scandium (Sc), calcium (Ca), magnesium (Mg), strontium (Sr), and barium (Ba), bismuth (Bi). These carboxylates, acetylacetonates and alcoholates can be readily formulated into a typical polyol pre-mix. Specifically, any metal carboxylates, acetylacetonates and alcoholates having one or more functional groups may be employed in the catalysts of the present invention. Such metal carboxylates, acetylacetonates and alcoholates may include, for example, magnesium formate, magnesium benzoate, magnesium octoate, calcium formate, calcium octoate, zinc octoate, cobalt octoate, and stannous octoate, zinc acetylacetonate, cobalt acetylacetonates, magnesium acetylacetonate, calcium acetylacetonate. Optionally, a solvent such as, for example, ethylene glycol, diethylene glycol, and toluene, may be utilized to dissolve the metal salts for mixing with the polyol pre-mix composition. Additionally, it is surprising and unexpected that the foams produced by mixing a polyol pre-mix composition of the present invention with a polyisocyanate have a uniform cell structure with little or no foam collapse.

DETAILED DESCRIPTION OF CERTAIN EMBODIMENTS OF THE INVENTION

Polyurethane foaming was studied by using halogenated olefins such as hydrochlorofluoroolefin 1-chloro-3,3,3-trifluoropropene, commonly referred to as HCFO-1233zd. The blends for polyurethane foam include a polyol, a surfactant, an amine catalyst, a halogenated olefin blowing agent, and a metal salt. It is now surprisingly found that the metal salt used in the present invention results in the improved stability of the foam blends over time. Additionally, the resultant foams were surprisingly found to have a uniform cell structure with little or no foam collapse.

Without being held to the theory, it is believed that the problem of the diminished shelf-life stability of the two-component systems, especially those using HCFO-1233zd, is related to the reaction of the halogenated olefins with the catalyst,

such as an amine catalyst. The reaction produces hydrofluoric acid (HF) which attacks the silicone surfactant *in situ*. This side reaction was confirmed by hydrogen, fluorine, and silicon nuclear magnetic resonance (NMR) spectra and gas chromatography-mass spectrometry (GC-MS). This effect can be summarized as the Nucleophilic attack of the catalyst, for example an amine catalyst, on the C_1 of the HCFO-1233zd halogenated olefin. Accordingly, the embodiments of the present invention reduce such detrimental interaction by decreasing the reactivity of the HCFO-1233zd halogenated olefin with the catalyst. Without being held to any theory, the reduction in degradation of the olefin caused by the catalyst is thought to be tied to the metal salts acting to protect the halogenated olefin blowing agent. This protective functionality of the metal salts prevents the detrimental interaction of the catalyst with halogenated olefins such as HCFO-1233zd, and the resulting HF production. The metal salts may also function as scavengers for hydrofluoric acid. In this way, the metal salts "clean-up" any HF that is produced by the reaction of the halogenated olefins with the catalyst, such as by the reaction with an amine catalyst.

The inventors of the present invention have now found that metal salts, such as metal carboxylates, metal acetylacetonates, metal alcoholates, for example, alkali earth carboxylates, alkali earth acetylacetonates and alcoholates, alkali carboxylates, alkali acetylacetonates and alcoholates, and carboxylates, acetylacetonates and alcoholates of zinc (Zn), cobalt (Co), tin (Sn), cerium (Ce), lanthanum (La), aluminum (Al), vanadium (V), manganese (Mn), copper (Cu), nickel (Ni), iron (Fe), titanium (Ti), zirconium (Zr), chromium (Cr), scandium (Sc), calcium (Ca), magnesium (Mg), strontium (Sr), and barium (Ba), bismuth (Bi) have good hydrofluoric acid (HF) scavenger activity and function to stabilize the polyol blends. For example, metal carboxylates having one or more functional carboxyl groups may be employed. The metal carboxylate may comprise a metal salt of a C1-C21 carboxylic acid. For example, the metal carboxylate may comprise a metal salt of a C1-C21 straight chain or branched aliphatic monocarboxylic acid. Similarly, a metal alcoholate may be employed such as, for example, a metal alcoholate which comprises a metal salt of a C1-C21 alcohol. The metal alcoholate may comprise a metal salt of a C1-C21 straight chain or branched aliphatic alcohol. Suitable carboxylic acids include, but are not limited to, formic acid, octanoic acid, 2-ethylhexanoic acid and the like. Suitable alcohols include methanol, ethanol, isopropanol, and the like. In one embodiment, the metal carboxylate comprises a

carboxylate of a metal selected from the group consisting of Zn, Co, Ca, and Mg. Suitable metal carboxylates may include, for example, magnesium formate, magnesium benzoate, magnesium octoate, calcium formate, calcium octoate, zinc octoate, cobalt octoate, stannous octoate, zinc acetylacetonate, cobalt acetylacetonate, magnesium acetylacetonate, and calcium acetylacetonate.

Generally speaking, an amount of one or more metal salts is utilized which is effective to improve the stability of the polyol pre-mix composition over the stability observed in the same composition in the absence of any metal salts and/or to improve the quality of the foam obtained by combining the polyol pre-mix composition with an A side comprised of polyisocyanate as compared to the foam quality obtained in the absence of any metal salts. Such amount may vary depending upon the details of a particular formulation, including, for example, the types and amounts of blowing agent, catalyst, and surfactant utilized as well as the particular metal salt(s) selected, but may be readily determined by routine experimentation. Typically, however, an amount of metal salt which is at least about 0.1% or at least about 0.3% by weight, based on the total weight of the polyol pre-mix composition will be suitable. Generally speaking, it is unnecessary to employ a metal salt content of greater than about 10% or about 5% by weight based on the total weight of the polyol pre-mix composition. For example, the polyol pre-mix composition may contain about 0.1 to about 10% by weight or about 0.3 to about 5% by weight metal salt based on the total weight of the polyol pre-mix composition. The metal salt(s) may, for example, be combined with the other components of the pre-mix composition in dry or solution form.

The present invention thus provides a polyol pre-mix composition which comprises a blowing agent, a polyol, a surfactant, a catalyst composition, and a metal salt. The catalyst composition may comprise an amine catalyst or a non-amine catalyst. In another embodiment the present invention provides a stabilized thermosetting foam blend which comprises: (a) a polyisocyanate and, optionally, isocyanate compatible raw materials; and (b) a polyol pre-mix composition which comprises a blowing agent, a polyol, a surfactant, a catalyst composition, and a metal salt. The catalyst composition may comprise an amine catalyst or a non-amine catalyst. In yet another embodiment, the present invention is a method for stabilizing thermosetting foam blends which comprises combining: (a) a polyisocyanate and, optionally, isocyanate compatible raw materials; and (b) a polyol pre-mix

composition which comprises a blowing agent, a polyol, a surfactant, a catalyst composition, and a metal salt. The catalyst composition may comprise an amine catalyst or a non-amine catalyst. The mixture according to this method produces a stable foamable thermosetting composition which can be used to form polyurethane or polyisocyanurate foams.

The metal salt of the present invention may be employed in polyol pre-mix compositions containing various amine catalysts. Traditional amine catalysts have been tertiary amines, such as triethylenediamine (TEDA), dimethylcyclohexylamine (DMCHA), and dimethylethanolamine (DMEA). Amine catalysts are generally selected based on whether they drive the gelling reaction or the blowing reaction. In the gelling reaction, polyfunctional isocyanates react with polyols to form polyurethane. In the blowing reaction, the isocyanate reacts with water to form polyurea and carbon dioxide. Amine catalysts can also drive the isocyanate trimerization reaction. These reactions take place at different rates; both reaction rates are dependent on temperature, catalyst level, catalyst type and a variety of other factors. However, to produce high-quality foam, the rates of the competing gelling and blowing reactions must be properly balanced. If the blowing reaction occurs faster than the gelling reaction, the gas generated by the reaction may expand before the polymer is strong enough to contain it and internal splits or foam collapse can occur. In contrast, if the gelling occurs faster than the blowing reaction, the foam cells will remain closed, causing the foam to shrink as it cools. Molecular structure gives some clue to the strength and selectivity of the catalyst. Blow catalysts generally have an ether linkage two carbons away from a tertiary nitrogen. Strong gel catalysts may contain alkyl-substituted nitrogens, while weaker gel catalysts may contain ring-substituted nitrogens. Trimerization catalysts may contain the triazine structure, or are quaternary ammonium salts. Catalysts that contain a hydroxyl group or an active amino hydrogen may also be employed.

As described above, catalysts function to control and balance the gelling and blowing reactions. Tertiary amine catalysts have their own specific catalytic characteristics such as gelling, blowing, and crosslinking activity. As would be appreciated by one having ordinary skill in the art, these catalytic activities have a strong relationship with rise profile, blowing efficiency, moldability, productivity, and other properties of the resulting foam. Accordingly, the polyol pre-mix compositions of the present invention include metal salt in addition to a variety of amine catalysts to

balance the blow, gel, and trimerization catalysis reactions and produce a foam having the desired properties. For example, the polyol pre-mix composition of the present invention may contain one or more metal salts in combination with one or more oxygen-containing amine catalysts. The polyol pre-mix composition of the present invention may alternatively, or additionally, include one or more non-oxygen-containing amine catalysts and/or non-amine catalysts.

The oxygen-containing amine catalysts which may be used in the present invention include those amines containing ether and/or a hydroxyl group. For example, the oxygen-containing amine catalyst may be an alkanolamine, ether amine or a morpholine group-containing catalyst such as an N-alkyl substituted morpholine. The catalyst may contain one, two, three or more nitrogen atoms in the form of amine functional groups. In one embodiment, all of the amine groups present in the catalyst molecule are tertiary amine groups. The catalyst, in one embodiment, may contain two, three or more oxygen atoms; these oxygen atoms may be present in the form of ether groups, hydroxyl groups or both ether and hydroxyl groups. Suitable oxygen-containing amine catalysts include compounds corresponding to the following chemical structure:

$R^1R^2N(CH_2)_2X(CH_2)_2Y$

wherein R^1 and R^2 are the same or different and are each a C_1-C_6 alkyl group, such as methyl, and /or an alkanol group, such as $-CH_2CH_2OH$ or $CH_2CH(CH_3)OH$; X is O, OH, or NR^3, where R^3 is a C_1-C_6 alkyl group, such as methyl, or an alkanol group, such as $-CH_2CH_2OH$ or $CH_2CH(CH_3)OH$; and Y is OH or NR^4R^5, where R^4 and R^5 are the same or different and are each a C_1-C_6 alkyl group, such as methyl, and/or an alkanol group such as $-CH_2CH_2OH$ or $-CH_2CH(CH_3)OH$; subject to the proviso that the compound contains at least one ether and/or hydroxyl group.

Exemplary oxygen-containing amine catalysts include:

bis-(2-dimethylaminoethyl)ether;

N,N-dimethylethanolamine;

N-ethylmorpholine;

N-methylmorpholine;

N,N,N'-trimethyl-N'-hydroxyethyl-bisaminoethylether;

N-(3-dimethylaminopropyl)-N,N-diisopropanolamine;

N,N-bis(3-dimethylaminopropyl)-N-isopropanolamine;

2-(2-dimethylaminoethoxy)ethanol;

N,N,N'-trimethylaminoethyl-ethanolamine; and

2,2'-dimorpholinodiethylether, and mixtures thereof.

Exemplary amine catalysts include: N-(3-dimethylaminopropyl)-N,N-diisopropanolamine, N,N-bis(3-dimethylaminopropyl)-N-isopropanolamine, 1,3-propanediamine, N'-(3-dimethylamino)propyl-N,N-dimethyl-, triethylenediamine, 1,2-dimethylimidazole, 1,3-propanediamine,N'-(3-(dimethylamino)propyl)-N,N-dimethyl-, N,N,N'N'-tetramethylhexanediamine, N,N'',N''-trimethylaminoethylpiperazine, 1-methyl-4-(2-dimethylaminoethyl)piperazine, N,N,N',N'tetramethylethylenediamine, N,N-dimethylcyclohexylamine (DMCHA), Bis(N,N-dimethylaminoethyl)ether (BDMAFE), 1,4-diazabicyclo[2,2,2]octane (DABCO), 2-((2-dimethylaminoethoxy)-ethyl methyl-amino)ethanol, 1-(bis(3-dimethylamino)-propyl)amino-2-propanol, N,N',N''-tris(3-dimethylamino-propyl)hexahydrotriazine, 1,3,5-tris(3-(dimethylamino)propyl-hexahydro-s-triazine, dimorpholinodiethylether (DMDEE), N.N-dimethylbenzylamine, N,N,N',N",N"-pentaamethyldipropylenetriamine, N,N'-diethylpiperazine, dicyclohexylmethylamine, ethyldiisopropylamine, dimethylcyclohexylamine, dimethylisopropylamine, methylisopropylbenzylamine, methylcyclopentylbenzylamine, isopropyl-sec-butyl-trifluoroethylamine, diethyl-(α-phenyethyl)amine, tri-n-propylamine, dicyclohexylamine, t-butylisopropylamine, di-t-butylamine, cyclohexyl-t-butylamine, de-sec-butylamine, dicyclopentylamine, di-(α-trifluoromethylethyl)amine, di-(α-phenylethyl)amine, triphenylmethylamine, and 1,1-diethyl-n-propylamine. Other amines include morpholines, imidazoles, ether containing compounds such as dimorpholinodiethylether, N-ethylmorpholine, N-methylmorpholine, bis(dimethylaminoethyl)ether, imidizole, n-methylimidazole, 1,2-dimethylimidazole, dimorpholinodimethylether, N,N,N',N',N",N"-pentamethyldipropylenetriamine, and bis(diethylaminoethyl)ether, bis(dimethylaminopropyl)ether, dimethylpiperazine, diethylaminopropylamine, ethylaminoethanol, diethylaminoethanol, isopropylaminoethanol, butylaminoethanol, dibutylaminoethanol, butyldiethanolamine, tert-butylaminoethanol, diethylhydroxylamine, and combinations thereof.

Exemplary non-amine catalysts include organometallic compounds containing bismuth, lead, tin, antimony, cadmium, cobalt, iron, thorium, aluminum, mercury,

zinc, nickel, cerium, molybdenum, titanium, vanadium, copper, manganese, zirconium, magnesium, calcium, sodium, potassium, lithium or combination thereof such as stannous octoate, dibutyltin dilaurate (DGTDL), dibutyltin mercaptide, phenylmercuric propionate, lead octoate, potassium acetate/octoate, magnesium acetate, titanyl oxalate, potassium titanyl oxalate, quaternary ammonium formates, and ferric acetylacetonate, and combinations thereof.

Bismuth and zinc carboxylates may be favorably employed over mercury and lead based catalysts, due to the toxicity and the necessity to dispose of mercury and lead catalysts and catalyzed material as hazardous waste in the United States, however these may have shortcomings in pot life and in certain weather conditions or applications. Alkyl tin carboxylates, oxides and mercaptides oxides are used in all types of polyurethane applications. Organometallic catalysts are useful in two-component polyurethane systems. These catalysts are designed to be highly selective toward the isocyanate-hydroxyl reaction as opposed to the isocyanate-water reaction, thus avoiding bubble generation at low levels of moisture.

As would be appreciated by one having ordinary skill in the art, the catalysts of the present invention may be selected, based on the various factors such as temperature, to produce balanced gelling and blowing reaction rates. Balancing the two competing reactions will produce high-quality foam structure. An ordinarily skilled artisan would further appreciate that the catalysts of the present invention may be employed alone, or in combination with organometallic catalysts, to achieve the desired functional properties and characteristics of the resulting foam structure. This includes, but is not limited to, other catalysts that have gelling or blowing reaction functionality.

The blowing agent in the thermosetting foam blends in one embodiment of the present invention includes an unsaturated halogenated hydroolefin such as a hydrofluoroolefin (HFO), hydrochlorofluoroolefin (HCFO), or mixtures thereof, and, optionally, one or more hydrofluorocarbons (HFCs), hydrofluoroether s (HFEs), hydrocarbons, alcohols, aldehydes, ketones, ethers/diethers or carbon dioxide generating materials. The preferred blowing agent in the thermosetting foam blend of the present invention is a hydrofluoroolefin (HFO) or a hydrochlorofluoroolefin (HCFO), alone or in a combination. 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 (HFO1234ye); trifluoropropenes, such as 3,3,3-trifluoropropene (1243zf); tetrafluorobutenes, such as (HFO 1345); pentafluorobutene isomers, such as (HFO1354); hexafluorobutene isomers, such as (HFO1336); heptafluorobutene isomers, such as (HFO1327); heptafluoropentene isomers, such as (HFO1447); octafluoropentene isomers, such as (HFO1438); nonafluoropentene isomers, such as (HFO1429); and hydrochlorofluoroolefins, such as 1-chloro-3,3,3-trifluoropropene (HCFO-1233zd) (E and Z isomers), 2-chloro-3,3,3-trifluoropropene (HCFO-1233xf), HCFO1223, 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). Preferred blowing agents in the thermosetting foam blends of the present invention include unsaturated halogenated hydroolefins with normal boiling points less than about 60°C. Preferred hydrochlorofluoroolefin blowing agents include, but are not limited to, 1-chloro-3,3,3-trifluoropropene; E and/or Z 1233zd; 1,3,3,3-tetrafluopropene; and E and/or Z 1234ze.

The halogenated olefinic blowing agents in the thermosetting foam blend of the present invention can be used alone or in combination with other blowing agents, including but not limited to:

(a) hydrofluorocarbons including but not limited to difluoromethane (HFC32); 1,1,1,2,2-pentafluoroethane (HFC125); 1,1,1-trifluoroethane (HFC143a); 1,1,2,2-tetrafluorothane (HFC134); 1,1,1,2-tetrafluoroethane (HFC134a); 1,1-difluoroethane (HFC152a); 1,1,1,2,3,3,3-heptafluoropropane (HFC227ea); 1,1,1,3,3-pentafluopropane (HFC245fa); 1,1,1,3,3-pentafluobutane (HFC365mfc) and 1,1,1,2,2,3,4,5,5,5-decafluoropentane (HFC4310mee),

(b) hydrocarbons including but not limited to, pentane isomers and butane isomers;

(c) hydrofluoroethers (HFE) such as, $C_4F_9OCH_3$ (HFE-7100), $C_4F_9OC_2H_5$ (HFE-7200), $CF_3CF_2OCH_3$ (HFE-245cb2), $CF_3CH_2CHF_2$ (HFE-245fa), $CF_3CH_2OCF_3$ (HFE-236fa), $C_3F_7OCH_3$ (HFE-7000), 2-trifluoromethyl-3-ethoxydodecofluorohexane (HFE 7500), 1,1,1,2,3-hexafluoro-4-(1,1,2,3,3,3-hexafluoropropoxy)-pentane (HFE-7600), 1,1,1,2,2,3,5,5,5-decafluoro-3-methoxy-4-(trifluoromethyl)pentane (HFE-7300), ethyl nonafluoroisobutyl ether/ethyl

nonafluorobutyl ether (HFE 8200), CHF_2OCHF_2, CHF_2-OCH_2F, CH_2F-OCH_2F, CH_2F-O-CH_3, cyclo-$CF_2CH_2CF_2$-O, cyclo-$CF_2CF_2CH_2$-O, CHF_2-CF_2CHF_2, CF_3CF_2-OCH_2F, CHF_2-O-$CHFCF_3$, CHF_2-OCF_2CHF_2, CH_2F-O-CF_2CHF_2, CF_3-O-CF_2CH_3, CHF_2CHF-O-CHF_2, CF_3-O-$CHFCH_2F$, CF_3CHF-O-CH_2F, CF_3-O-CH_2CHF_2, CHF_2-O-CH_2CF_3, CH_2FCF_2-O-CH_2F, CHF2-O-CF_2CH_3, CHF_2CF_2-O-CH_3 (HFE254pc), CH_2F-O-$CHFCH_2F$, CHF_2-CHF-O-CH_2F, CF_3-O-$CHFCH_3$, CF_3CHF-O-CH_3, CHF_2-O-CH_2CHF_2, CF_3-O-CH_2CH_2F, CF_3CH_2-O-CH_2F, $CF_2HCF_2CF_2$-O-CH_3, CF_3CHFCF_2-O-CH_3, $CHF_2CF_2CF_2$-O-CH_3, $CHF_2CF_2CH_2$-$OCHF_2$, $CF_3CF_2CH_2$-O-CH_3, CHF_2CF_2-O-CH_2CH_3, $(CF_3)_2CF$-O-CH_3, $(CF_3)_2CH$-O-CHF_2, and $(CF_3)_2CH$-O-CH_3, and mixtures thereof; and

(d) C1 to C5 alcohols, C1 to C4 aldehydes, C1 to C4 ketones, C1 to C4 ethers and diethers and carbon dioxide generating materials.

The thermosetting foam blends of the present invention include one or more components capable of forming foam having a generally cellular structure and blowing agent(s). Examples of thermosetting compositions include polyurethane and polyisocyanurate foam compositions, preferably low-density foams, flexible or rigid.

The invention also relates to foam, and preferably closed cell foam, prepared from a thermosetting foam formulation to which has been added a stabilizing amount of an ester. When an ester is employed, the order and manner in which the blowing agent and ester combination of the present invention is formed and/or added to the foamable composition does not generally affect the operability of the present invention. For example, in the case of polyurethane foams, it is possible that the various components of the blowing agent and ester combination not be mixed in advance of introduction to the foaming equipment, or even that the components are not added to the same location in the foaming equipment. Thus, in certain embodiments it may be desired to introduce one or more components of the blowing agent and ester combination in such a way that the components will come together in the foaming equipment. Nevertheless, in certain embodiments, the components of the blowing agent and ester combination are combined in advance and introduced together into the foamable composition, either directly or as part of a pre-mix that is then further added to other parts of the foamable composition.

In certain embodiments in the preparation of polyurethane polyol foams, the B-side polyol pre-mix composition can include polyols, silicone or non-silicone based surfactants, catalysts, flame retardants or suppressors, acid scavengers, radical

scavengers, fillers, and other stabilizers or inhibitors. The catalysts may include an amine catalyst or a non-amine catalyst.

The polyol component, which can include mixtures of polyols, can be any polyol which reacts in a known fashion with an isocyanate in preparing a polyurethane or polyisocyanurate foam. Exemplary polyols include: glycerin-based polyether polyols such as Carpol® GP-700, GP-725, GP-4000, GP-4520; amine-based polyether polyols such as Carpol® TEAP-265 and EDAP-770, Jeffol® AD-310; sucrose-based polyether polyols, such as Jeffol® SD-360, SG-361,and SD-522, Voranol® 490, and Carpol® SPA-357; Mannich-based polyether polyols, such as Jeffol® R-425X and R-470X; sorbitol-based polyether polyols, such as Jeffol® S-490; and aromatic polyester polyols such as Terate® 2541 and 3510, Stepanpol® PS-2352, and Terol® TR-925.

The polyol pre-mix composition may also contain a surfactant. The surfactant is used to form a foam from the mixture, as well as to control the size of the bubbles of the foam so that a foam of a desired cell structure is obtained. Preferably, a foam with small bubbles or cells therein of uniform size is desired since it has the most desirable physical properties such as compressive strength and thermal conductivity. Also, it is critical to have a foam with stable cells which do not collapse prior to foaming or during foam rise. Silicone surfactants for use in the preparation of polyurethane or polyisocyanurate foams are available under a number of trade names known to those skilled in this art. Such materials have been found to be applicable over a wide range of formulations allowing uniform cell formation and maximum gas entrapment to achieve very low density foam structures.

Exemplary silicone surfactants include polysiloxane polyoxyalkylene block co-polymer such as B8404, B8407, B8409, B8462 and B8465 available from Goldschmidt; DC-193, DC-197, DC-5582, and DC-5598 available from Air Products; and L-5130, L5180, L-5340, L-5440, L-6100, L-6900, L-6980, and L6988 available from Momentive. Exemplary non-silicone surfactants include salts of sulfonic acid, alkali metal salts of fatty acids, ammonium salts of fatty acids, oleic acid, stearic acid, dodecylbenzenedisulfonic acid, dinaphthylmetanedisulfonic acid, ricinoleic acid, an oxyethylated alkylphenol, an oxyethylated fatty alcohol, a paraffin oil, a caster oil ester, a ricinoleic acid ester, Turkey red oil, groundnut oil, a paraffin fatty alcohol, or combinations thereof. Typical use levels of surfactants are from about 0.4 to 6 wt% of polyol pre-mix, preferably from about 0.8 to 4.5wt%, and more preferably from

about 1 to 3 wt%.

Exemplary flame retardants include trichloropropyl phosphate (TCPP), triethyl phosphate (TEP), diethyl ethyl phosphate (DEEP), diethyl bis (2-hydroxyethyl) amino methyl phosphonate, brominated anhydride based ester, dibromoneopentyl glycol, brominated polyether polyol, melamine, ammonium polyphosphate, aluminum trihydrate (ATH), tris(1,3-dichloroisopropyl) phosphate, tri(2-chloroethyl) phosphate, tri(2-chloroisopropyl) phosphate, chloroalkyl phosphate/oligomeric phosphonate, oligomeric chloroalkyl phosphate, brominated flame retardant based on pentabromo diphenyl ether, dimethyl methyl phosphonate, diethyl N,N bis(2-hydroxyethyl) amino methyl phosphonate, oligomeric phosphonate, and derivatives thereof.

In certain embodiments, acid scavengers, radical scavengers, and/or other stabilizers/inhibitors are included in the pre-mix. Exemplary stabilizer/inhibitors include 1,2-epoxy butane; glycidyl methyl ether; cyclic-terpenes such as dl-limonene, l-limonene, d-limonene; 1,2-epoxy-2,2-methylpropane; nitromethane; diethylhydroxyl amine; alpha methylstyrene; isoprene; p-methoxyphenol; m-methoxyphenol; dl-limonene oxide; hydrazines; 2,6-di-t-butyl phenol; hydroquinone; organic acids such as carboxylic acid, dicarboxylic acid, phosphonic acid, sulfonic acid, sulfamic acid, hydroxamic acid, formic acid, acetic acid, propionic acid, butyric acid, caproic acid, isocaprotic acid, 2-ethylhexanoic acid, caprylic acid, cyanoacetic acid, pyruvic acid, benzoic acid, oxalic acid, malonic acid, succinic acid, adipic acid, azelaic acid, trifluoroacetic acid, methanesulfonic acid, benzenesulfonic acid, and combinations thereof. Other additives such as adhesion promoters, anti-static agents, antioxidants, fillers, hydrolysis agents, lubricants, anti-microbial agents, pigments, viscosity modifiers, UV resistance agents may also be included. Examples of these additives include: sterically hindered phenols; diphenylamines; benzofuranone derivatives; butylated hydroxytoluene (BHT); calcium carbonate; barium sulphate; glass fibers; carbon fibers; micro-spheres; silicas; melamine; carbon black; waxes and soaps; organometallic derivatives of antimony, copper, and arsenic; titanium dioxide; chromium oxide; iron oxide; glycol ethers; dimethyl AGS esters; propylene carbonate; and benzophenone and benzotriazole compounds.

In some embodiments of the present invention, an ester may be added to a thermosetting foam blend. The addition of an ester was surprisingly discovered to further improve the stability of the blend over time, as in extending shelf life of the pre-mix, and enhancing the properties of the resultant foam. Esters useful in the

present invention may have the formula R-C(O)-O-R', where R and R' can be $C_aH_{c-b}G_b$, where G is a halogen such as F, Cl, Br, I, a=0 to 15, b= 0 to 31, and c=1 to 31, and include esters that are the products obtained by esterification of dicarboxylic acid, phosphinic acid, phosphonic acid, sulfonic acid, sulfamic acid, hydroxamic acid or combinations thereof. Preferred esters are the products obtained by esterification using an alcohol such as methanol, ethanol, ethylene glycol, diethylene glycol, propanol, isopropanol, butanol, iso-butanol, pentanol, iso-pentanol and mixtures thereof; and an acid such as formic, acetic, propionic, butyric, caproic, isocaprotic, 2-ethylhexanoic, caprylic, cyanoacetic, pyruvic, benzoic, oxalic,trifluoacetic,oxalic, malonic, succinic, adipic, azelaic, trifluoroacetic, methanesulfonic, benzene sulfonic acid and mixture thereof. The more preferred esters are allyl hexanoate, benzyl acetate, benzyl formate, bornyl acetate, butyl butyrate, ethyl acetate, ethyl butyrate, ethyl hexanoate, ethyl cinnamate, ethyl formate, ethyl heptanoate, ethyl isovalerate, ethyl lactate, ethyl nonanoate, ethyl pentanoate, geranyl acetate, geranyl butyrate, geranyl pentanoate, isobutyl acetate, isobutyl formate, isoamyl acetate, isopropyl acetate, linalyl acetate, linalyl butyrate, linalyl formate, methyl acetate, methyl anthranilate, methyl benzoate, methyl butyrate, methyl cinnamate, methyl formate, methyl pentanoate, methyl propanoate, methyl phenylacetate, methyl salicylate, nonyl caprylate, octyl acetate, octyl butyrate, amyl acetate/pentyl acetate, pentyl butyrate/amyl butyrate, pentyl hexanoate/amyl caproate, pentyl pentanoate/amyl valerate, propyl ethanoate, propyl isobutyrate, terpenyl butyrate and mixtures thereof. Most preferred esters are methyl formate, ethyl formate, methyl acetate, and ethyl acetate, and mixtures thereof.

The ester can be added in combination with the blowing agent, or can be added separately from the blowing agent into the thermosetting foam blend by various means known in art. The typical amount of an ester is from about 0.1 wt% to 10 wt% of thermosetting foam blend, the preferred amount of an ester is from about 0.2 wt% to 7 wt% of thermosetting foam blend, and the more preferred amount of an ester is from about 0.3 wt% to 5 wt% of thermosetting foam blend.

The preparation of polyurethane or polyisocyanurate foams using the compositions described herein may follow any of the methods well known in the art can be employed, see Saunders and Frisch, Volumes I and II Polyurethanes Chemistry and technology, 1962, John Wiley and Sons, New York, N.Y. or Gum, Reese, Ulrich, 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, polyurethane or polyisocyanurate foams are prepared by combining an isocyanate, the polyol pre-mix composition, and other materials such as optional flame retardants, colorants, or other additives. These foams 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.

It is convenient in many applications to provide the components for polyurethane or polyisocyanurate foams in pre-blended formulations. Most typically, the foam formulation is pre-blended into two components. The isocyanate and optionally other isocyanate compatible raw materials comprise the first component, commonly referred to as the "A-" side component. The polyol mixture composition, including surfactant, catalysts, blowing agents, and optional other ingredients comprise the second component, commonly referred to as the "B-" side component. In any given application, the "B-" side component may not contain all the above listed components, for example some formulations omit the flame retardant if that characteristic is not a required foam property. Accordingly, polyurethane or polyisocyanurate foams are readily prepared by bringing together the A- and B-side components either by hand mix for small preparations and, preferably, machine mix techniques to form blocks, slabs, laminates, pour-in-place panels and other items, spray applied foams, froths, and the like. Optionally, other ingredients such as fire retardants, colorants, auxiliary blowing agents, water, and even other polyols can be added as a stream to the mix head or reaction site. Most conveniently, however, they are all incorporated into one B-side component as described above. In some circumstances, A and B can be formulated and mixed into one component in which water is removed. Polymerization occurs when the one-component mixture is discharged and exposed to air. This is typical, for example, for a spray-foam canister containing a one-component foam mixture for easy application.

A foamable composition suitable for forming a polyurethane or polyisocyanurate foam may be formed by reacting an organic polyisocyanate and the polyol premix composition described above. Any organic polyisocyanate can be employed in polyurethane or polyisocyanurate foam synthesis inclusive of aliphatic and aromatic polyisocyanates. Suitable organic polyisocyanates include aliphatic, cycloaliphatic, araliphatic, aromatic, and heterocyclic isocyanates which are well known in the field of polyurethane chemistry.

EXAMPLES

The invention is further illustrated by reference to the following Examples.

Example 1

Example 1 shows the improved stability imparted by the use of a metal salt, such as an alkali earth salt of a carboxylic acid, which have good hydrofluoric acid (HF) scavenger activity and impart stability to the polyol pre-mix composition. Magnesium formate is employed in this example, but other metal salts, such as, for example, alkali earth carboxylates, alkali earth acetylacetonate, alkali carboxylates, alkali acetylacetonate, and carboxylates, acetylacetonates, and alcoholates of zinc (Zn), cobalt (Co), tin (Sn), cerium (Ce), lanthanum (La), aluminum (Al), vanadium (V), manganese (Mn), copper (Cu), nickel (Ni), iron (Fe), titanium (Ti), zirconium (Zr), chromium (Cr), scandium (Sc), calcium (Ca), magnesium (Mg), strontium (Sr), barium (Ba), and bismuth (Bi) can be employed according to the present invention to improve the stability of the polyol pre-mix composition.

An aqueous formulation was prepared by mixing together: 2 wt% pentamethyldiethylenetriamine (PMDETA), 4 wt% of a silicon surfactant (TEGOSTAB® B 8465), 2 wt% magnesium formate, and 92 wt% of a hydrochlorofluoroolefin (HCFO) HCFO-1233zd "E" halogenated olefinic blowing agent. For comparison, a solution without magnesium formate was prepared by mixing together: 2 wt% pentamethyldiethylenetriamine (PMDETA), 4 wt% of a silicon surfactant (TEGOSTAB® B 8465), and 94 wt% of a hydrochlorofluoroolefin (HCFO) HCFO-1233zd "E" halogenated olefinic blowing agent. The two mixtures were then aged at 50°C for 15 days in an oven. Each sample was mixed with a solution of deuterated chloroform ($CDCl_3$) solvent. The blends were then analyzed to obtain NMR spectra at 25 °C, acquired on a Bruker DRX 500 (11.7 T) spectrometer equipped with a 5 mm TBI probe. The small amount of products related to the interaction between the HCFO-1233zd "E" and the amine and silicon surfactant can be normalized to the HCFO-1233zd "E" and therefore quantified. The results of this comparison are summarized in Table 1 below.

Table 1. Comparison of formulations with and without the use of a metal salt.

	Product related to the amine (%)	Product related to the surfactant (%)
Without Magnesium Formate	100	100
With Magnesium Formate	3	8

As Table 1 shows, magnesium formate can suppress the formation of products by the detrimental interaction between hydrochlorofluoroolefin (HCFO) HCFO-1233zd "E" halogenated olefinic blowing agent and the amine and the surfactant. Example 1 shows that metal salts, such as an alkali earth salt of a carboxylic acid, have good hydrofluoric acid (HF) scavenger activity and improve the stability of the polyol pre-mix composition.

Example 2

Example 2 shows a comparative B-side pre-mix formulation which does not include a metal salt. The comparative B-side component was pre-blended according to the formulation shown in Table 2 below. The B-side component included an aqueous blend of polyols, such as those sold by Dow Chemical under the trade name Voranol 490, those sold by Huntsman under the trade name Jeffol R-425-X, and those sold by Stepan Company under the trade name Stepanpol PS-2352; a silicone surfactant sold under the trade name TEGOSTAB® B 8465 by Evonik Industries - Degussa; and amine catalysts, specifically dimethylcyclohexylamine sold under the trade name POLYCAT® 8 and pentamethyldiethylenetriamine sold under the trade name POLYCAT® 5, both of which are available from Air Products and Chemicals, Inc. The B-side component also included Antiblaze 80, a flame retardant from Rhodia.

Table 2. Comparative Formulation of Example 2.

COMPONENT	Wt % of Total
Voranol 490	36.77
Jeffol R-425-X	22.06
Stepanol 2352	14.71
Polycat 5	0.33

Polycat 8	1.06
Tegostab B8465	1.51
Antiblaze 80	4.98
Water	1.57
E1233zd	17.01
Total	100.00
A-side / B-side	**1.11**

The formulation tested (which had an ISO Index of 115) contained a polymeric methylene diphenyl diisocyanate (MDI) sold by Huntsman under the trade name Rubinate M as the A-side component. In this example, the A-side component, which is a polymeric methylene diphenyl diisocyanate (MDI), and the B-side component, which is a blend of the polyol, surfactant, catalysts, blowing agent, and additives, were mixed with a hand mixer and dispensed into a container to form a free rise foam. The total blowing level was 23.0 ml/g. Three samples were prepared according to the above formulation and aged for different periods of time and different conditions: an unaged sample, a sample aged for 15 days at ambient temperature, and a sample aged for 15 days at 50°C. Properties such as cream, gel, and tack free times, free rise density (FRD), and foam quality were measured, which are summarized in Table 3 below:

Table 3. Measured properties for aged formulation of Example 2.

Measured Properties	Unaged Sample	Aged 15 days @ Ambient Temp	Aged 15 days @ 50°C
Cream time, sec	10	10	16
Gel time, sec	36	41	55
Tack free time, sec	68	83	-----*
Free Rise Density (pcf)	1.84	1.80	-----*
Foam quality	Good	Good	Poor

* Could not be measured due to poor foam quality.

As shown in Table 3 above, ageing the polyol pre-mix composition formulation of

Example 2 had a detrimental effect on foam quality. The sample aged for 15 days at 50°C was found to have increased detrimental effect on foam quality, indicating that both the catalysts and the surfactant lost almost all of their functional properties. Accordingly, the comparative formulation of Example 2 was found to have poor shelf-life stability and performance characteristics.

Example 3

Example 3 shows an exemplary formulation of the present invention, in which the B-side polyol pre-mix composition includes 2.9 wt % of a cobalt octoate solution (25 wt % in an organic solvent) as a metal salt stabilizer. The cobalt octoate metal salt solution was added to the formulation and measured according to the procedure described in Example 2 above. The resulting properties are summarized in Table 4 below:

Table 4. Measured properties for aged formulation of Example 3.

Measured Properties	Unaged Sample	Aged 15 days @ 50°C
Cream time, sec	13	14
Gel time, sec	42	48
Tack free time, sec	82	71
Free Rise Density (pcf)	1.72	1.77
Foam quality	Good	Coarse

As shown in Table 4 above, ageing the polyol pre-mix formulation of Example 3 also had an effect on foam quality. The sample aged for 15 days at 50°C was found to have an increased effect on foam quality. The aged sample containing cobalt octoate metal salt had much less effect, however, on foam catalysis as the cream, gel, and free rise density only increased slightly when compared to the unaged sample.

Example 4

Example 4 shows an exemplary formulation of the present invention, in which the B-side polyol pre-mix composition includes 2.9 wt % of a potassium octoate as a metal salt stabilizer. The potassium octoate metal salt solution was added to the

formulation and measured according to the procedure described in Example 2 above. The resulting properties are summarized in Table 5 below:

Table 5. Measured properties of the aged formulation of Example 4.

Measured Properties	Unaged Sample	Aged 15 days @ 50°C
Cream time, sec	10	15
Gel time, sec	35	45
Tack free time, sec	56	58
Free Rise Density (pcf)	1.73	-----*
Foam quality	Good	Poor

* Could not be measured due to poor foam quality.

As shown in Table 5 above, ageing the polyol pre-mix formulation of Example 4 showed a much detrimental effect on foam quality. The sample aged for 15 days at 50°C was found to have increased detrimental effect on foam quality, indicating that both the catalysts and the blowing agent lost almost all of their functional properties.

Example 5

Example 5 shows an exemplary formulation of the present invention, in which the B-side polyol pre-mix composition includes 2.9 wt % of a zinc octoate solution as a metal salt stabilizer. The zinc octoate metal salt solution was added to the formulation and measured according to the procedure described in Example 2 above. The resulting properties are summarized in Table 6 below:

Table 6. Measured properties of the aged formulation of Example 5.

Measured Properties	Unaged Sample	Aged 15 days @ 50°C
Cream time, sec	11	13
Gel time, sec	32	44
Tack free time, sec	62	100
Free Rise Density (pcf)	1.74	1.78

Foam quality	Good	Good

As shown in Table 6 above, ageing the polyol blend formulation of Example 5 had only a small effect on foam quality. The sample aged for 15 days at 50°C was found to have much less effect on foam quality and foam catalysis, when compared to the comparative formulation, as shown by the cream and gel time measurements. The cream and gel time of the aged sample increased only slightly over the unaged sample, indicating that the halogenated olefin blowing agent was protected by the addition of the zinc octoate metal salt stabilizer.

Example 6

Example 6 shows an exemplary formulation of the present invention, in which the B-side polyol blend includes 2.9 wt % of a magnesium octoate solution (2-ethylhexonate) as a metal salt stabilizer. The magnesium octoate metal salt solution was added to the formulation and measured according to the procedure described in Example 2 above. The resulting properties are summarized in Table 7 below:

Table 7. Measured properties of the aged formulation of Example 6.

Measured Properties	Unaged Sample	Aged 15 days @ 50°C
Cream time, sec	11	15
Gel time, sec	40	55
Tack free time, sec	83	69
Free Rise Density (pcf)	1.77	-----*
Foam quality	Good	Poor

* Could not be measured due to poor foam quality.

As shown in Table 7 above, the aged polyol blend formulation of Example 6 showed a detrimental effect on foam quality. The sample aged for 15 days at 50°C was found to have increased detrimental effects on foam quality, indicating that the blowing agent lost almost all of its functional properties.

Example 7

Example 7 shows an exemplary formulation of the present invention, in which the B-side polyol blend includes 2.9 wt % of a calcium octoate solution (2-ethylhexonate) as a metal salt stabilizer. The magnesium octoate metal salt solution was added to the formulation and measured according to the procedure described in Example 2 above. The resulting properties are summarized in Table 8 below:

Table 8. Measured properties of the aged formulation of Example 7.

Measured Properties	Unaged Sample	Aged 15 days @ 50°C
Cream time, sec	11	15
Gel time, sec	36	64
Tack free time, sec	67	155
Free Rise Density (pcf)	1.75	1.80
Foam quality	Good	Fair to Good

As shown in Table 8 above, the aged polyol blend formulation of Example 7 showed a lesser detrimental effect on foam quality. The sample aged for 15 days at 50°C was found to have much less effect on foam quality, indicating that the halogenated olefin blowing agent was protected by addition of the stabilizer.

Example 1 employed magnesium formate as a HF scavenger and stabilizer. Metal salts, such as metal carboxylates, metal acetylacetonates, metal alcoholates, for example, alkali earth carboxylates, alkali earth acetylacetonates and alcoholates, alkali carboxylates, alkali acetylacetonates and alcoholates, and carboxylates, acetylacetonates and alcoholates of zinc (Zn), cobalt (Co), tin (Sn), cerium (Ce), lanthanum (La), aluminum (Al), vanadium (V), manganese (Mn), copper (Cu), nickel (Ni), iron (Fe), titanium (Ti), zirconium (Zr), chromium (Cr), scandium (Sc), calcium (Ca), magnesium (Mg), strontium (Sr), and barium (Ba), bismuth (Bi) have good hydrofluoric acid (HF) scavenger activity and function to stabilize the polyol blends. For example, metal carboxylates having one or more functional carboxyl groups may be employed. The metal carboxylate may comprise a metal salt of a C1-C21 carboxylic acid. For example, the metal carboxylate may comprise a metal salt of a C1-C21 straight chain or branched aliphatic monocarboxylic acid. Similarly, a metal alcoholate may be employed such as, for example, a metal alcoholate which

comprises a metal salt of a C1-C21 alcohol. The metal alcoholate may comprise a metal salt of a C1-C21 straight chain or branched aliphatic alcohol. Suitable carboxylic acids include, but are not limited to, formic acid, octanoic acid, 2-ethylhexanoic acid and the like. Suitable alcohols include methanol, ethanol, isopropanol, and the like. In one embodiment, the metal salt comprises a carboxylate of a metal selected from the group consisting of Zn, Co, Ca, and Mg. Suitable metal carboxylates may include, for example, magnesium formate, magnesium benzoate, magnesium octoate, calcium formate, calcium octoate, zinc octoate, cobalt octoate, stannous octoate, zinc acetylacetonate, cobalt acetylacetonate, magnesium acetylacetonate, and calcium acetylacetonate. The metal salts may be utilized in polyol blends which contain oxygen-containing amine catalyst, as shown in Example 1, or other amine catalysts, as shown in Examples 2-7, or with non-amine catalysts. While certain of the metal salts function better than others, all of the polyol blend formulations of the present invention which contain metal salts showed better stability and less detrimental interaction between the halogenated olefin and catalysts than the polyol blends which lack such metal salts.

Although the invention is illustrated and described herein with reference to specific embodiments, the invention is not intended to be limited to the details shown. Rather, various modifications may be made in the details within the scope and range of equivalents of the claims and without departing from the invention.

What is claimed is:

1. A polyol pre-mix composition comprising a blowing agent comprising a halogenated hydroolefin, a polyol, a surfactant, a catalyst composition comprising an amine catalyst or non-amine catalyst, and a metal salt.

2. The polyol pre-mix composition of claim 1, wherein the catalyst composition comprises an oxygen-containing amine catalyst.

3. The polyol pre-mix composition of claim 2, wherein the oxygen-containing amine catalyst is an alkanolamine, ether amine, or a morpholine group-containing catalyst.

4. The polyol pre-mix composition of claim 2, wherein the oxygen-containing amine catalyst is a compound having the chemical structure:

$R^1R^2N(CH_2)_2X(CH_2)_2Y$

wherein:

R^1 and R^2 are the same or different and are each a C_1-C_6 alkyl group and/or an alkanol group,

X is O, OH, or NR^3, where R^3 is a C_1-C_6 alkyl group or an alkanol group, and

Y is OH or NR^4R^5, where R^4 and R^5 are the same or different and are each a C_1-C_6 alkyl group or an alkanol group, subject to the proviso that the compound contains at least one ether and/or hydroxyl group.

5. The polyol pre-mix composition of claim 1, wherein the catalyst composition comprises a non-oxygen-containing amine catalyst.

6. The polyol pre-mix composition of claim 1, wherein the catalyst composition comprises a non-amine catalyst.

7. The polyol pre-mix composition of claim 6, wherein the non-amine catalyst comprises an organometallic complex of tin (Sn) or lead (Pb) or mixtures thereof.

8. The polyol pre-mix composition of claim 1, wherein the blowing agent additionally comprises one or more hydrofluorocarbons (HFCs), hydrofluoroethers (HFEs), hydrocarbons, alcohols, aldehydes, ketones, ethers/diethers, or CO_2 generating materials, or combinations thereof.

9. The polyol pre-mix composition of claim 1, wherein the blowing agent comprises a halogenated hydroolefin selected from the group consisting of hydrofluoroolefins (HFOs), hydrochlorofluoroolefins (HCFOs), and mixtures thereof, and optionally one or more hydrofluorocarbons (HFCs), hydrofluoroethers (HFEs), hydrocarbons, alcohols, aldehydes, ketones, ethers/diethers, esters, or carbon dioxide generating materials.

10. The polyol pre-mix composition of claim 1, wherein the surfactant comprises a polysiloxane polyoxyalkylene block co-polymer silicone surfactant.

11. The polyol pre-mix composition of claim 1, wherein the pre-mix composition is comprised of from about 0.3 to about 5 weight percent of one or more metal carboxylates, acetylacetonates, and alcoholates based on the total weight of the polyol pre-mix composition.

12. The polyol pre-mix composition of claim 1, wherein the metal salt comprises a carboxylate and/or alcoholate of a metal selected from the group consisting of Zn, Co, Ca, and Mg.

13. The polyol pre-mix composition of claim 1, wherein the metal salt comprises a carboxylate and/or alcoholate of a C1-C21 carboxylic acid or alcohol.

14. The polyol pre-mix composition of claim 1, wherein the metal salt comprises a carboxylate and/or alcoholate of a C1-C21 straight chain or branched aliphatic monocarboxylic acid or monoalcohol.

15. The polyol pre-mix composition of claim 1, wherein the metal salt is selected from the group consisting of magnesium formate, zinc octoate, calcium octoate, cobalt octoate, and magnesium octoate, and mixtures thereof.

16. The polyol pre-mix composition of claim 1, wherein the metal salt is selected from the group consisting of magnesium acetylacetonate, zinc acetylacetonate, calcium acetylacetonate, cobalt acetylacetonate, and mixtures thereof.

17. A two-part system for producing a thermosetting foam blend, wherein the system comprises:

(a) as a first part, a polyisocyanate and, optionally, one or more isocyanate compatible raw materials; and

(b) as a second part, a polyol pre-mix composition which comprises a blowing agent comprising a halogenated hydroolefin, a polyol, a surfactant, a catalyst composition comprising an amine or non-amine catalyst, and a metal salt.

18. The two-part system of claim 17, wherein the catalyst composition includes an oxygen-containing amine catalyst.

19. The two-part system of claim 18, wherein the oxygen-containing amine catalyst is an alkanolamine, ether amine, or a morpholine group-containing catalyst.

20. The two-part system of claim 17, wherein the catalyst composition comprises a non-oxygen-containing amine catalyst.

21. The two-part system of claim 17, wherein the blowing agent comprises a halogenated hydroolefin selected from the group consisting of hydrofluoroolefins (HFOs), hydrochlorofluoroolefins (HCFOs), and mixtures thereof, and optionally one or more hydrofluorocarbons (HFCs), hydrofluoroethers (HFEs), hydrocarbons, alcohols, aldehydes, ketones, ethers/diethers, or CO_2 generating materials, or combinations thereof.

22. The two-part system of claim 17, wherein the pre-mix composition is comprised of from about 0.3 to about 5 weight percent of one or more metal carboxylates and/or acetylacetonates.

23. The two-part system of claim 17, wherein the metal salt comprises a carboxylate and/or acetylacetonate of a metal selected from the group consisting of Zn, Co, Ca, and Mg.

24. The two-part system of claim 17, wherein the metal salt comprises a carboxylate and/or alcoholate of a C1-C21 carboxylic acid or alcohol.

25. The two-part system of claim 17, wherein the metal salt comprises a carboxylate and/or alcoholate of a C1-C21 straight chain or branched aliphatic monocarboxylic acid or monoalcohol.

26. The two-part system of claim 17, wherein the metal salt is selected from the group consisting of magnesium formate, zinc octoate, calcium octoate, cobalt octoate, and magnesium octoate, and mixtures thereof.

27. The two-part system of claim 17, wherein the metal salt is selected from the group consisting of magnesium acetylacetonate, zinc acetylacetonate, calcium acetylacetonate, cobalt acetylacetonate, and mixtures thereof.

28. A method for producing a thermosetting foam blend which comprises combining: (a) a polyisocyanate and, optionally, one or more isocyanate compatible raw materials; and (b) a polyol pre-mix composition which comprises a blowing agent comprising a halogenated hydroolefin, a polyol, a surfactant, a catalyst composition comprising an amine or non-amine catalyst, and a metal salt.

29. The method of claim 28, wherein the catalyst composition includes an oxygen-containing amine catalyst.

30. The method of claim 29, wherein the oxygen-containing amine catalyst is a compound having the chemical structure:

$R^1R^2N(CH_2)_2X(CH_2)_2Y$

wherein:

R^1 and R^2 are the same or different and are each a C_1-C_6 alkyl group and/or an alkanol group,

X is O, OH, or NR^3, where R^3 is a C_1-C_6 alkyl group or an alkanol group, and

Y is OH or NR^4R^5, where R^4 and R^5 are the same or different and are each a C_1-C_6 alkyl group or an alkanol group, subject to the proviso that the compound contains at least one ether and/or hydroxyl group.

31. The method of claim 28, wherein the catalyst composition comprises a non-oxygen-containing amine catalyst.

32. The method of claim 28, wherein non-amine catalyst composition comprises an organometallic complex of tin (Sn) or lead (Pb) or mixtures thereof.

33. The method of claim 28, wherein the blowing agent comprises a halogenated hydroolefin selected from the group consisting of hydrofluoroolefins (HFOs), hydrochloroolefins (HCFOs), and mixtures thereof, and, optionally, one or more hydrofluorocarbons (HFCs), hydrofluoroethers (HFEs), hydrocarbons, alcohols, aldehydes, ketones, ethers/diethers, esters, or CO_2 generating materials, or combinations thereof.

34. A mixture suitable for providing a polyurethane or polyisocyanurate foam having uniform cell structure with little or no foam collapse, wherein the mixture comprises: (a) a polyisocyanate and, optionally, one or more isocyanate compatible raw materials; and (b) a polyol pre-mix composition which comprises a blowing agent comprising a halogenated hydroolefin, a polyol, a surfactant, a catalyst composition comprising an amine catalyst or non-amine catalyst, and a metal salt.

35. A polyol pre-mix composition comprising a blowing agent comprising a halogenated hydroolefin, a polyol, a surfactant, a catalyst composition comprising an amine catalyst, and a metal salt.

36. The polyol pre-mix composition of claim 35, wherein the catalyst composition comprises an oxygen-containing amine catalyst.

37. The polyol pre-mix composition of claim 36, wherein the oxygen-containing amine catalyst is an alkanolamine, ether amine, or a morpholine group-containing catalyst.

38. The polyol pre-mix composition of claim 36, wherein the oxygen-containing amine catalyst is a compound having the chemical structure:

$R^1R^2N(CH_2)_2X(CH_2)_2Y$

wherein:

R^1 and R^2 are the same or different and are each a C_1-C_6 alkyl group and/or an alkanol group,

X is O, OH, or NR^3, where R^3 is a C_1-C_6 alkyl group or an alkanol group, and

Y is OH or NR^4R^5, where R^4 and R^5 are the same or different and are each a C_1-C_6 alkyl group or an alkanol group, subject to the proviso that the compound contains at least one ether and/or hydroxyl group.

39. The polyol pre-mix composition of claim 35, wherein the catalyst composition comprises a non-oxygen-containing amine catalyst.

40. The polyol pre-mix composition of claim 35, wherein the blowing agent additionally comprises one or more hydrofluorocarbons (HFCs), hydrofluoroethers (HFEs), hydrocarbons, alcohols, aldehydes, ketones, ethers/diethers, or CO_2 generating materials, or combinations thereof.

41. The polyol pre-mix composition of claim 35, wherein the blowing agent comprises a halogenated hydroolefin selected from the group consisting of hydrofluoroolefins (HFOs), hydrochlorofluoroolefins (HCFOs), and mixtures thereof, and optionally one or more hydrofluorocarbons (HFCs), hydrofluoroethers (HFEs), hydrocarbons, alcohols, aldehydes, ketones, ethers/diethers, esters, or carbon dioxide generating materials.

42. The polyol pre-mix composition of claim 35, wherein the surfactant comprises a polysiloxane polyoxyalkylene block co-polymer silicone surfactant.

43. The polyol pre-mix composition of claim 35, wherein the pre-mix composition is comprised of from about 0.3 to about 5 weight percent of one or more metal carboxylates, acetylacetonates, and alcoholates based on the total weight of the polyol pre-mix composition.

44. The polyol pre-mix composition of claim 35, wherein the metal salt comprises a carboxylate and/or alcoholate of a metal selected from the group consisting of Zn, Co, Ca, and Mg.

45. The polyol pre-mix composition of claim 35, wherein the metal salt comprises a carboxylate and/or alcoholate of a C1-C21 carboxylic acid or alcohol.

46. The polyol pre-mix composition of claim 35, wherein the metal salt comprises a carboxylate and/or alcoholate of a C1-C21 straight chain or branched aliphatic monocarboxylic acid or monoalcohol.

47. The polyol pre-mix composition of claim 35, wherein the metal salt is selected from the group consisting of magnesium formate, zinc octoate, calcium octoate, cobalt octoate, and magnesium octoate, and mixtures thereof.

48. The polyol pre-mix composition of claim 35, wherein the metal salt is selected from the group consisting of magnesium acetylacetonate, zinc acetylacetonate, calcium acetylacetonate, cobalt acetylacetonate, and mixtures thereof.

49. A two-part system for producing a thermosetting foam blend, wherein the system comprises:

(a) as a first part, a polyisocyanate and, optionally, one or more isocyanate compatible raw materials; and

(b) as a second part, a polyol pre-mix composition which comprises a blowing agent comprising a halogenated hydroolefin, a polyol, a surfactant, a catalyst composition comprising an amine catalyst, and a metal salt.

50. The two-part system of claim 49, wherein the catalyst composition includes an oxygen-containing amine catalyst.

51. The two-part system of claim 50, wherein the oxygen-containing amine catalyst is an alkanolamine, ether amine, or a morpholine group-containing catalyst.

52. The two-part system of claim 49, wherein the catalyst composition comprises a non-oxygen-containing amine catalyst.

53. The two-part system of claim 49, wherein the blowing agent comprises a halogenated hydroolefin selected from the group consisting of hydrofluoroolefins (HFOs), hydrochlorofluoroolefins (HCFOs), and mixtures thereof, and optionally one or more hydrofluorocarbons (HFCs), hydrofluoroethers (HFEs), hydrocarbons, alcohols, aldehydes, ketones, ethers/diethers, or CO_2 generating materials, or combinations thereof.

54. The two-part system of claim 49, wherein the pre-mix composition is comprised of from about 0.3 to about 5 weight percent of one or more metal carboxylates and/or acetylacetonates.

55. The two-part system of claim 49, wherein the metal salt comprises a carboxylate and/or acetylacetonate of a metal selected from the group consisting of Zn, Co, Ca, and Mg.

56. The two-part system of claim 49, wherein the metal salt comprises a carboxylate and/or alcoholate of a C1-C21 carboxylic acid or alcohol.

57. The two-part system of claim 49, wherein the metal salt comprises a carboxylate and/or alcoholate of a C1-C21 straight chain or branched aliphatic monocarboxylic acid or monoalcohol.

58. The two-part system of claim 49, wherein the metal salt is selected from the group consisting of magnesium formate, zinc octoate, calcium octoate, cobalt octoate, and magnesium octoate, and mixtures thereof.

59. The two-part system of claim 49, wherein the metal salt is selected from the group consisting of magnesium acetylacetonate, zinc acetylacetonate, calcium acetylacetonate, cobalt acetylacetonate, and mixtures thereof.

60. A method for producing a thermosetting foam blend which comprises combining: (a) a polyisocyanate and, optionally, one or more isocyanate compatible raw materials; and (b) a polyol pre-mix composition which comprises a blowing agent comprising a halogenated hydroolefin, a polyol, a surfactant, a catalyst composition comprising an amine catalyst, and a metal salt.

61. The method of claim 60, wherein the catalyst composition includes an oxygen-containing amine catalyst.

62. The method of claim 61, wherein the oxygen-containing amine catalyst is a compound having the chemical structure:

$R^1R^2N(CH_2)_2X(CH_2)_2Y$

wherein:

R^1 and R^2 are the same or different and are each a C_1-C_6 alkyl group and/or an alkanol group,

X is O, OH, or NR^3, where R^3 is a C_1-C_6 alkyl group or an alkanol group, and

Y is OH or NR^4R^5, where R^4 and R^5 are the same or different and are each a C_1-C_6 alkyl group or an alkanol group, subject to the proviso that the compound contains at least one ether and/or hydroxyl group.

63. The method of claim 60, wherein the catalyst composition comprises a non-oxygen-containing amine catalyst.

64. The method of claim 60, wherein the blowing agent comprises a halogenated hydroolefin selected from the group consisting of hydrofluoroolefins (HFOs), hydrochloroolefins (HCFOs), and mixtures thereof, and, optionally, one or more hydrofluorocarbons (HFCs), hydrofluoroethers (HFEs), hydrocarbons, alcohols, aldehydes, ketones, ethers/diethers, esters, or CO_2 generating materials, or combinations thereof.

65. A mixture suitable for providing a polyurethane or polyisocyanurate foam having uniform cell structure with little or no foam collapse, wherein the mixture comprises: (a) a polyisocyanate and, optionally, one or more isocyanate compatible raw materials; and (b) a polyol pre-mix composition which comprises a blowing agent comprising a halogenated hydroolefin, a polyol, a surfactant, a catalyst composition comprising an amine catalyst, and a metal salt.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 12/27802

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - C08G 65/26; C08G 18/38; C08G 18/50 (2012.01)
USPC - 521/137; 521/138; 521/164; 521/170; 521/171; 521/1
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) - C08G 65/26; C08G 18/38; C08G 18/50 (2012.01)
USPC - 521/137; 521/138; 521/164; 521/170; 521/171; 521/1

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
IPC(8) - C08G 65/26; C08G 18/38; C08G 18/50 (2012.01)
USPC - 521/137; 521/138; 521/164; 521/170; 521/171; 521/1 (keyword delimited)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PubWEST (PGPB,USPT,USOC,EPAB,JPAB) Terms - halogen halogenated olefin blowing polyol magnesium zinc calcium cobalt octoate acetylacetonate carboxylate foam Honeywell
Google - polyurethane polyol halogenated-olefin blowing agent (octoate OR acetylacetonate)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2009/0099272 A1 (WILIAMS, ET AL.) 16 April 2009 (16.04.2009), entire document, especially, para [0003], [0013], [0016]-[0029], [0041])	1-65
X,P	US 2011/0152392 A1 (VAN DER PUY, ET AL.) 23 June 2011 (23.06.2011), entire document	1-65
A	US 2011/0039964 A1 (WILIAMS, ET AL.) 17 February 2011 (17.02.2011), entire document	1-65
A	US 2009/0270522 A1 (SINGH, ET AL.) 29 October 2009 (29.10.2009), entire document	1-65
A	US 2009/0099273 A1 (WILIAMS, ET AL.) 16 April 2009 (16.04.2009), entire document	1-65

☐ 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
12 June 2012 (12.06.2012)	19 JUN 2012
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774