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(54) Titre : COMPOSITIONS D'AGENT D'EXPANSION CONTENANT DU 1,2,2-TRIFLUORO-1-TRIFLUOROMETHYLCYCLOBUTANE, ET PROCEDES D'EXPANSION
(54) Title: FOAMING AGENT COMPOSITIONS CONTAINING 1,2,2-TRIFLUORO-1-TRIFLUOROMETHYLCYCLOBUTANE, AND METHODS OF FOAMING

(57) Abrégé/Abstract:

A blowing agent composition includes a blowing agent and a nucleating agent. The nucleating agent includes 1,2,2-trifluoro-1-trifluoromethylcyclobutane. The 1,2,2-trifluoro-1-trifluoromethylcyclobutane is present in the blowing agent composition in an amount from about 0.5 wt.% to about 7 wt.% of the blowing agent composition.

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(54) Title: FOAMING AGENT COMPOSITIONS CONTAINING 1,2,2-TRIFLUORO-1-TRIFLUOROMETHYLCYCLOBUTANE, AND METHODS OF FOAMING

(57) Abstract: A blowing agent composition includes a blowing agent and a nucleating agent. The nucleating agent includes 1,2,2-trifluoro-1-trifluoromethylcyclobutane. The 1,2,2-trifluoro-1-trifluoromethylcyclobutane is present in the blowing agent composition in an amount from about 0.5 wt.% to about 7 wt.% of the blowing agent composition.

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FOAMING AGENT COMPOSITIONS CONTAINING 1,2,2-TRIFLUORO-1-TRIFLUOROMETHYLCYCLOBUTANE, AND METHODS OF FOAMING

FIELD

[0001] The present disclosure is related to blowing agent compositions comprising 1,2,2-trifluoro-1-trifluoromethylcyclobutane (TFMCB), methods for foaming using these compositions, and foams comprising these compositions.

BACKGROUND

[0002] Fluorocarbon fluids have properties that are desirable for use in a variety of applications, including as blowing agents, and other applications. Unfortunately, the use of certain hydrofluorocarbons "HFCs" in industrial applications is now believed to contribute to the global warming, and accordingly, have limited their contemporary use. However, the identification of new, environmentally-safe compositions comprising HFCs is complicated, due to the fact that many properties which make them useful in these applications are not readily predictable. For example, it is desirable that blowing agent compositions not only have acceptable environmental properties, but also chemical stability, low- or no- toxicity, low or no-flammability, among others. It is also desirable that the blowing agent has excellent performance when in use, e.g. excellent thermal insulating properties and other desirable foam characteristics.

[0003] Therefore, the industry is continually seeking new HFC-based mixtures that are acceptable and environmentally safer substitutes to the incumbent compositions.

[0004] Methods and compositions for making conventional foamed materials, such as for example thermoplastic materials and thermosetting materials, have long been known. These methods and compositions have typically utilized chemical and/or physical blowing agents to form the foamed structure in a polymeric matrix. Such blowing agents have included, for example, azo compounds, various volatile organic compounds (VOCs) and chlorofluorocarbons (CFCs). The chemical blowing agents typically undergo some form of chemical change, including chemical reaction with the material that forms the polymer matrix (usually at a predetermined temperature/pressure) that causes the release of a gas, such as nitrogen, carbon dioxide, or carbon monoxide. One of the most frequently used chemical blowing agents is water. The physical blowing agents typically are dissolved in the polymer or polymer precursor material and then expand volumetrically (again at a predetermined temperature/pressure) to contribute to the formation of the foamed structure. Physical blowing agents are frequently used in connection with thermoplastic foams, although chemical blowing agents can be used in place of or in addition to physical blowing agents in connection with thermoplastic foam. For example, it is known to use chemical blowing agent in connection with the formation of polyvinylchloride-based foams. It is common to use chemical blowing and/or physical blowing agents in connection with thermosetting foams. Of course, it is possible that certain compounds and the compositions that contain them may at once constitute a chemical and a physical blowing agent.

[0005] It was common in the past that the CFCs were used as standard blowing agents in the preparation of isocyanate-based foams, such as rigid and flexible polyurethane and polyisocyanurate foams. For example, CCl_3F (CFC-11) had become a standard blowing agent. However, the use of this material has been banned by international treaty on the grounds that its release into the atmosphere damages the ozone layer in the stratosphere. As a consequence, it is no longer generally common that neat CFC-11 is used as a standard blowing agent for forming thermosetting foams, such as isocyanate-based foams and phenolic foams.

[0006] The problems with CFCs led to the more frequent utilization hydrogen-containing chlorofluoroalkanes (HCFCs). For example, $CHCl_2CF_3$ (HCFC-123), $CH_2ClCHClF$ (HCFC-141b) have relatively short lifetimes in the atmosphere. However, while HCFCs are considered to be environmentally friendly blowing agents relative to CFCs, such compounds still contain some chlorine, and therefore have an "Ozone Depletion Potential" (called "ODP"). Because of the non-zero ODP, HCFCs have been targeted for eventual removal from use.

[0007] Another known class of blowing agents is the non-chlorinated, partially hydrogenated fluorocarbons (called "HFCs"). Certain of the HFC currently being used as blowing agents have at least one potentially serious problem, namely that they generally have relatively high intrinsic thermal conductivity properties (i.e., poor thermal insulation). On the other hand, foams made with certain of the more modern HFC blowing agents, such as $CF_3CH_2CF_2H$ (“HFC-245fa”) offer improved thermal insulation, due in part to the low thermal conductivity of HFC-245fa vapor, and due in part to the fine cell structure HFC-245fa imparts to the foams. HFC-245fa has been widely used in insulation applications, particularly refrigerator, freezer, refrigerator/freezer and spray foam applications. Nevertheless, many HFC fluids share the disadvantage of having relatively high global warming potentials, and it is desirable to use hydrofluorocarbon or other fluorinated fluids having as low global warming potentials as possible while maintaining the desired performance in use properties. Even the more modern HFCs, such as HFC-245fa, HFC-134a, HFC-365mfc, and others, exhibit a higher than desirable global warming potential, albeit low relative to other HFCs. Thus, the use of high global warming potential HFCs as blowing agents in foam insulation, particularly rigid foam insulation, has resulted in HFCs being less desirable candidates for blowing agents in commercial foam insulation.

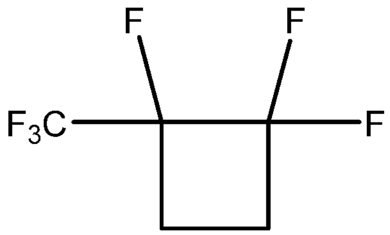
[0008] There has thus been an increasing need for new compounds and compositions that are attractive alternatives to the compositions heretofore used as blowing agents in these and other applications.

[0009] Applicants have thus come to appreciate a need for compositions, and particularly blowing agents, foamable compositions, foamed articles and methods and systems for forming foam, which provide beneficial properties and/or avoid one or more of the disadvantages noted above.

SUMMARY

[0010] Applicants have found that the above-noted needs, and other needs, can be satisfied by methods, processes and the use of blowing agent compositions, foamable compositions, foams and/or foamed articles comprising 1,2,2-trifluoro-1-trifluoromethylcyclobutane (TFMCB).

[0011] The compound 1,2,2-trifluoro-1-trifluoromethylcyclobutane ("TFMCB") has the following chemical structure:



[0012] 1,2,2-trifluoro-1-trifluoromethylcyclobutane ("TFMCB") may also be referred to by alternative names, including 1,2,2-trifluoro-1-trifluoromethyl cyclobutane, 1-trifluoromethyl-1,2,2-trifluorocyclobutane, 1,1,2-trifluoro-2-trifluoromethyl-cyclobutane, or hexafluoropropylene/ethylene cyclic dimer.

[0013] TFMCB may be manufactured by any appropriate method. Suitable methods include those set out in US-A-9856193 and US-A-10005705, the entire of which are hereby incorporated by reference.

[0014] "Global Warming Potential" (hereinafter "GWP") was developed to allow comparisons of the global warming impact of different gases. It is a measure of how much energy the emission of one ton of a gas will absorb over a given period of time, relative to the emission of one ton of carbon dioxide. The larger GWP, the more that a given gas warms the Earth compared to CO_2 over that time period. The time period usually used for GWP is 100 years. GWP provides a common measure, which allows analysts to add up emission estimates of different gases. See Intergovernmental Panel on Climate Change (IPCC) 5th Assessment Report (AR5), 2014. TFMCB has a GWP of 44 as calculated from the atmospheric lifetime and radiative efficiency (Reference for procedure: Hodnebrog, Etminan, Fuglestvedt, Marston, Myhre, Nielsen, Shine, Wallington "Global Warming

Potentials and Radiative Efficiencies of Halocarbons and Related Compounds: A Comprehensive Review" *Reviews of Geophysics*, 51, 2013. DOI: 8755-1209/13/10.1002/rog.20013. TFMCB has a GWP of about 44.

[0015] LC_{50} is a measure of the acute toxicity of a compound. The acute inhalation toxicity of a compound can be assessed using the method described in the OECD Guideline for Testing of Chemicals No. 403 "Acute Inhalation Toxicity" (2009), Method B.2. (Inhalation) of Commission Regulation (EC) No. 440/2008. TFMCB has an LC_{50} of > 19.15 mg/L.

[0016] Non-flammable in the context of a blowing agent composition means compounds or compositions which are determined to be non-flammable. The flash point of a solvent / blowing agent refers the lowest temperature at which vapors of the liquid will keep burning after the ignition source is removed as determined in accordance with ASTM D3828. Blowing agents which do not have a flash point below 100 °F (37.8 °C) are classified as "non-flammable" in accordance with NFPA 30: Flammable and Combustible Liquid Code.

[0017] TFMCB may be manufactured by any appropriate method. Suitable methods include those set out in US-A-9,856,193 and US-A-10,005,705, the entire disclosures of which are hereby incorporated by reference.

1. Blowing Agent Compositions

[0018] The present invention relates to a blowing agent composition comprising 1-trifluoromethyl-1,2,2-trifluorocyclobutane (TFMCB).

[0019] The blowing agent may comprise the TFMCB in an amount of at least about 7% by weight, preferably at least about 10% by weight, more preferably at least about 15% by weight, more preferably at least about 20% by weight, more preferably at least about 25% by weight, more preferably at least about 30% by weight of the blowing agent composition. more preferably at least about 40% by weight, more preferably at least about 50% by weight.

[0020] Alternatively, the blowing agent may consist essentially of TFMCB. Alternatively, the blowing agent may consist of TFMCB.

[0021] The blowing agent composition may comprise TFMCB in any of the amounts set out above in combination with one or more co-blowing agents.

[0022] The one or more co-blowing agents can be selected from the group consisting of HFC-152a, HFC-245fa, HFC-134, HFC-134a, HFC-365mfc, propane, butane, pentane, hexane, HFO-1234ze(E), HFO-1234yf, HFO-1336mzz(E), HFO-1336mzz(Z), HFO-1233zd(E), HFO-1233zd(Z), HFO-1224yd(E), HFO-1224yd(Z), C1-C4 alcohol, *trans*-dichloroethylene (*trans*-DCE), methyl formate, C1 – C4 aldehydes, C3 – C4 ketones, C2 – C4 ethers, diethers, water, CO_2, and combinations thereof.

[0023] When the blowing agent of the invention comprises butane, the butane can be selected from iso-and n-butane. Such blowing agents are particularly preferred for the production of a thermoplastic foam.

[0024] When the blowing agent of the invention comprises pentane, the pentane can be selected from iso-, normal-, neo-, and/or cyclopentane. Preferably the pentane is cyclopentane. Such blowing agents are particularly preferred for the production of a thermoset foam.

[0025] The hydrocarbon blowing agent (i.e. the propane, butane, pentane, hexane) is preferably present in the blowing agent in amounts of from about 5% by weight to about 80% by weight of the total blowing agent composition, and even more preferably from about 20% by weight to about 60% by weight of the total blowing agent.

[0026] When the blowing agent of the invention comprises a C1 to C4 alcohol, the alcohol can be selected from methanol, ethanol, propanol, isopropanol, butanol, isobutanol or t-butanol. Preferably the blowing agent comprises the alcohol in an amount of from about 5% by weight to about 40% by weight of the total blowing agent, more preferably from about 10% by weight to about 40% by weight, and even more preferably of from about 15% to about 25% by weight of the total blowing agent.

[0027] When the blowing agent of the invention comprises an ether or a diether, the ether can be dimethyl ether or diethyl ether and the diether can be dimethoxy methane or diethoxy ethane. Preferably the blowing agent comprises the ether in an amount of from about 5% by weight to about 40% by weight of the total blowing agent, more preferably from about 10% by weight to about 40% by weight, and even more preferably of from about 15% to about 25% by weight of the total blowing agent.

[0028] When the blowing agent of the invention comprises a C1-C4 aldehyde, the aldehyde can be selected from formaldehyde, acetaldehyde, propanal, butanal and isobutanal. Preferably the blowing agent comprises the aldehyde in an amount of from about 5% by weight to about 40% by weight of the total blowing agent, more preferably from about 10% by weight to about 40% by weight, and even more preferably of from about 15% to about 25% by weight of the total blowing agent.

[0029] When the blowing agent of the invention comprises a C3 to C4 ketone, the ketone can be selected from acetone, methylethylketone and methylisobutylketone. Preferably the blowing agent comprises the ketone in an amount of from about 5% by weight to about 40% by weight of the total blowing agent, more preferably from about 10% by weight to about 40% by weight, and even more preferably of from about 15% to about 25% by weight of the total blowing agent.

[0030] When the blowing agent of the invention comprises water, the blowing agent comprises H2O in an amount of from about 5% by weight to about 50% by weight of the total blowing agent composition, more preferably from about 10% by weight to about 40% by weight, and even more preferably of from about 10% to about 20% by weight of the total blowing agent.

[0031] When the blowing agent of the invention comprises methyl formate, the blowing agent comprises methyl formate in an amount of from about 5% by weight to about 50% by weight of the total blowing agent composition, more preferably from about 10% by weight to about 40% by weight, and even more preferably of from about 10% to about 20% by weight of the total blowing agent.

[0032] When the blowing agent of the invention comprises *trans*-dichloroethylene, the blowing agent comprises *trans*-dichloroethylene in an amount of from about 5% by weight to about 50% by weight of the total blowing agent composition, more preferably from about 10% by weight to about 40% by weight, and even more preferably of from about 10% to about 20% by weight of the total blowing agent.

[0033] When the blowing agent of the invention comprises methylal, the blowing agent comprises methylal in an amount of from about 5% by weight to about 50% by weight of the total blowing agent composition, more preferably from about 10% by weight to about 40% by weight, and even more preferably of from about 10% to about 20% by weight of the total blowing agent.

[0034] When the blowing agent comprises CO2, the blowing agent comprises CO2 in an amount of from about 5% by weight to about 60% by weight of the total blowing agent composition, more preferably from about 20% by weight to about 50% by weight, and even more preferably of from about 40% to about 50% by weight of the total blowing agent.

[0035] When the blowing agent comprises an HFC co-blowing agent, such as HFC-152a, HFC-245fa, HFC-134, HFC-134a, or HFC-365mfc, the HFC co-blowing agent is preferably present in the composition in amounts of from about 5% by weight to about 80% by weight of the total blowing agent composition, more preferably from about 10% by weight to about 75% by weight, and even more preferably of from about 25% to about 75% by weight of the total blowing agent, more preferably from about 20% by weight to about 60% by weight of the total blowing agent.

[0036] When the blowing agent comprises an HFO co-blowing agent, such as HFO-1234ze(E), HFO-1234yf, HFO-1336mzz(E), HFO-1336mzz(Z), HFO-1233zd(E), HFO-1233zd(Z), HFO-1224yd(E), HFO-1224yd(Z), the HFO co-blowing agent is preferably present in the composition in amounts of from about 5% by weight to about 80% by weight of the total blowing agent composition, more preferably from about 10% by weight to about 75% by weight, and even more preferably of from about 25% to about 75% by weight of the total blowing agent, more preferably from about 20% by weight to about 60% by weight of the total blowing agent.

[0037] It will be appreciated that the blowing agent composition may consist essentially of, or consist of the TFMCB and co-blowing agent.

[0038] The blowing agent composition preferably has a GWP of not greater than about 1000, more preferably not greater than about 500, more preferably not greater than about 150.

[0039] It has been surprisingly discovered that TFMCB is non-flammable. Thus, the blowing agent composition is preferably non-flammable.

2. Other Components

[0040] It is contemplated that the blowing agent compositions according to any embodiments of this disclosure may include additional components. Such optional additional compounds include, but are not limited to, surfactants, polymer modifiers, toughening agents, colorants, dyes, solubility enhancers, rheology modifiers, plasticizing agents, flammability suppressants, antibacterial agents, viscosity reduction modifiers, fillers, vapor pressure modifiers, catalysts, dispersing agents, cell stabilizers, surfactants etc.

[0041] Certain surfactants are optionally but preferably added to serve as cell stabilizers. Some representative materials are sold under the names of DC-193, B-8404, and L-5340 which are, generally, polysiloxane polyoxyalkylene block co-polymers such as those disclosed in U.S. Patent Nos. 2,834,748, 2,917,480, and 2,846,458, each of which is incorporated herein by reference. Other optional additives for the blowing agent mixture may include flame retardants such as tri(2-chloroethyl)phosphate, tri(2-chloropropyl)phosphate, tri(2,3-dibromopropyl)-phosphate, tri(1,3-dichloropropyl) phosphate, diammonium phosphate, various halogenated aromatic compounds, antimony oxide, aluminum trihydrate, polyvinyl chloride, and the like.

3. Foamable Compositions

[0042] The present invention provides foamable compositions including a blowing agent composition of the invention, and one or more components capable of forming foam.

[0043] As used herein, the term “foam foaming agent” is used to refer to a component, or a combination on components, which are capable of forming a foam structure, preferably a generally cellular foam structure.

[0044] The one or more components capable of forming foam may be a composition capable of forming a thermosetting foam. Examples of thermosetting foams include polyurethane and polyisocyanurate foam, and also phenolic foam.

[0045] It will also be appreciated that the one or more components capable of forming foam may be a composition capable for forming a thermoplastic foam. Thus, the one or more components capable of forming foam may be a thermoplastic polymer and/or resin. Examples of thermoplastic foams include polyolefins, such as for example monovinyl aromatic compounds of the formula Ar-CHCH2 wherein Ar is an aromatic hydrocarbon radical of the benzene series such as polystyrene (PS). Other examples of suitable polyolefin resins in accordance with the invention include the various ethylene resins including the ethylene homopolymers such as polyethylene and ethylene copolymers, polypropylene (PP) and polyethyleneterepthalate (PET). Thus, the thermoplastic foam may be a polyethylene (PE), polypropylene (PP), polystyrene (PS) or polyethyleneterepthalate (PET) foam.

[0046] When the foam is a thermoplastic foam, the foamable composition is preferably an extrudable composition. Thus, the foam is preferably an extruded thermoplastic foam. More preferably, the foam is preferably an extruded polystyrene foam.

[0047] Where the foam is a phenolic foam, it can be produced by foaming and curing a foamable phenolic resin composition comprising a phenolic resin, a catalyst, and optionally an inorganic filler with a blowing agent of the claimed invention.

4. The Foams

[0048] The invention also relates to a closed cell foam comprising the blowing agent composition of the invention.

[0049] The foam may be a rigid foam, a flexible foam, or an integral skin foam. Preferably, the invention relates to a closed cell rigid foam comprising the blowing agent composition of the invention.

[0050] The foam of the present invention can be a block, a slab, a laminate, a panel, such as a pour-in-place panel, a spray applied foam, a froth, and the like

[0051] Applicants have found that one advantage of the foams in accordance with the present invention is the ability to achieve exceptional thermal performance, such as can be measured by the K-factor or lambda.

[0052] Although it is contemplated that the present foams, particularly thermoset foams of the present invention, may be used in a wide variety of applications, in certain preferred embodiments the present invention comprises appliance foams in accordance with the present invention, including refrigerator foams, freezer foams, refrigerator/freezer foams, panel foams, and other cold or cryogenic manufacturing applications.

[0053] The foams of the present invention are particularly provided for use in appliance, refrigeration, transportation and building industries (for example as building envelopes).

[0054] The foams in accordance with the present invention provide one or more exceptional features, characteristics and/or properties, including: thermal insulation efficiency (particularly for thermoset foams), dimensional stability, compressive strength, aging of thermal insulation properties, all in addition to the low global warming potential associated with the blowing agents of the present invention.

[0055] Preferably the foams (and particularly the thermoset foams, of the present invention exhibit a K-factor (BTU in / hr ft^2 °F) at 40°F of not greater than about 0.14, more preferably not greater than 0.135, and even more preferably not greater than 0.13. Furthermore, it is preferred that the foams (particularly the thermoset foams, of the present invention exhibit a K-factor (BTU in / hr ft^2 °F) at 75°F of not greater than about 0.16, more preferably not greater than 0.15, and even more preferably not greater than 0.145.

[0056] The present foams may exhibit improved mechanical properties relative to foams produced with blowing agents outside the scope of the present invention. For example, the foams may have a compressive strength which is superior to, and preferably at least about 10 relative percent, and even more preferably at least about 15 relative percent greater than a foam produced under substantially identical conditions by utilizing a blowing agent consisting of cyclopentane. Furthermore, the foams may have compressive strengths that are on a commercial basis comparable to the compressive strength produced by making a foam under substantially the same conditions except wherein the blowing agent consists of HFC-245fa. The foams may exhibit a compressive strength of at least about 12.5% yield (in the parallel and perpendicular directions), and even more preferably at least about 13% yield in each of said directions.

[0057] The foam may be a thermoset foam or a thermoplastic foam. The thermoplastic foam is preferably polyethylene (PE), polypropylene (PP), polystyrene (PS) or polyethyleneterepthalate (PET). Preferably, the thermoplastic foam is an extruded thermoplastic foam. More particularly the foam is an extruded polystyrene foam.

[0058] When the foam is a thermoplastic foam, the blowing agent of the present invention preferably comprises TFMCB either alone or in combination with one or more of CO2, HFC-152a, HFC-245fa, HFC-134, HFC-134a, butane, isobutane, HFO-1234ze(E), HFO-1234yf, HFO-1336mzz(E), HFO-1336mzz(Z), HFO-1233zd(E), HFO-1233zd(Z), HFO-1224yd(E), HFO-1224yd(Z), ethanol, dimethylether, acetone, methyl formate, and methylal.

[0059] The thermoset foam is preferably a polyisocyanate, polyurethane or phenolic foam.

[0060] When the foam is a thermoset foam, the blowing agent of the present invention preferably comprises TFMCB either alone or in combination with one or more of water, CO2, methyl formate, methylal, HFO-1234ze(E), HFO-1234yf, HFO-1336mzz(E), HFO-1336mzz(Z), HFO-1233zd(E), HFO-1233zd(Z), HFO-1224yd(E), HFO-1224yd(Z), HFC-152a, formic acid, n-pentane, isopentane, cyclopentane, *trans* 1,2-dichloroethylene, HFC-245fa, HFC-365mfc, HFC-134a and HFC-134a.

[0061] The phenolic foam can be a resole resin obtained from the chemical reaction of an aldehyde and a phenol or phenol based compound.

5. Methods and Systems

[0062] It is contemplated that all presently known and available methods and systems for forming foam are readily adaptable for use in connection with the present invention. For example, the methods of the present invention generally require incorporating a blowing agent in accordance with the present invention into a foamable composition and then foaming the composition, preferably by a step or series of steps which include causing volumetric expansion of the blowing agent in accordance with the present invention. In general, it is contemplated that the presently used systems and devices for incorporation of blowing agent and for foaming can readily be used in accordance with the present invention. In fact, it is believed that one advantage of the present invention is the provision of an improved blowing agent which is generally compatible with existing foaming methods and systems.

[0063] Thus, it will be appreciated by those skilled in the art that the present invention comprises methods and systems for foaming all types of foams, including thermosetting foams, and thermoplastic foams. Thus, the present invention relates to the use of the present blowing agents in connection with conventional foaming equipment at conventional processing conditions. The present methods therefore include masterbatch type operations, blending type operations, third stream blowing agent addition, and blowing agent addition at the foam head.

[0064] With respect to thermoplastic foams, the preferred methods generally comprise introducing a blowing agent in accordance with the present invention into a thermoplastic material, preferably thermoplastic polymer, and then subjecting the thermoplastic material to conditions effective to cause foaming.

[0065] For example, the step of introducing the blowing agent into the thermoplastic material may comprise introducing the blowing agent into an extruder (e.g. a screw extruder) containing the thermoplastic, and the step of causing foaming may comprise lowering the pressure on the thermoplastic material and thereby causing expansion of the blowing agent and contributing to the foaming of the material.

[0066] It will be appreciated by those skilled in the art, especially in view of the disclosure contained herein, that the order and manner in which the blowing agent 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 extrudable foams, it is possible that the various components of the blowing agent, and even the components of the foamable composition, be not be mixed in advance of introduction to the extrusion equipment, or even that the components are not added to the same location in the extrusion equipment. Moreover, the blowing agent can be introduced either directly or as part of a premix, which is then further added to other parts of the foamable composition.

[0067] Thus, it may be desired to introduce one or more components of the blowing agent at first location in the extruder, which is upstream of the place of addition of one or more other components of the blowing agent, with the expectation that the components will come together in the extruder and/or operate more effectively in this manner. Nevertheless, it may be preferred that two or more components of the blowing agent are combined in advance and introduced together into the foamable composition, either directly or as part of premix which is then further added to other parts of the foamable composition.

[0068] The present invention also relates to methods of forming thermoset foams, and preferably polyurethane, polyisocyanurate or phenolic foams. The methods generally comprise providing a blowing agent composition of the present inventions, adding (directly or indirectly) the blowing agent composition to a foamable composition, and reacting the foamable composition under the conditions effective to form a foam or cellular structure, as is well known in the art. Any of the methods well known in the art, such as those described in “Polyurethanes Chemistry and Technology,” Volumes I and II, Saunders and Frisch, 1962, John Wiley and Sons, New York, NY, which is incorporated herein by reference, may be used in accordance with the present invention. In general, such preferred methods comprise preparing thermoset (e.g. polyurethane, or polyisocyanurate foams) by combining an isocyanate, a polyol or mixture of polyols, a blowing agent composition of the invention, and optionally other materials such as catalysts, surfactants, flame retardants, colorants, or other additives.

[0069] It is convenient to provide the components for polyurethane or polyisocyanurate foams in pre-blended formulations. Most typically, the pre-blended formulation is pre-blended into two components. The isocyanate and optionally certain surfactants comprise the first component, commonly referred to as the “A” component. The polyol or polyol mixture, optional surfactants, catalysts, flame retardants comprise the second component, commonly referred to as the “B” component. The blowing agent composition may be present in the A component and/or the B component. For example, if the blowing agent composition comprises two blowing agents, the first blowing agent may be present in the A component, and the second blowing agent may be present in the B component.

[0070] Accordingly, polyurethane or polyisocyanurate foams are readily prepared by bringing together the A and B side components by mixing to form a foam, for example blocks, slabs, laminates, pour-in-place panels and other items, spray applied foams, froths, and the like. The mixing may be by hand mix e.g. for small preparations or machine mixing techniques.

[0071] The present methods and systems also include forming a one component thermoset foam, preferably polyurethane foam, containing a blowing agent in accordance with the present invention. A portion of the blowing agent may be contained in the foam forming agent of the one component foam, preferably by being dissolved in the foam forming agent which is liquid at the pressure within the container, and a second portion of the blowing agent may be present as a separate gas phase. In such systems, the contained/dissolved blowing agent performs, in large part, to cause the expansion of the foam, and the separate gas phase operates to impart propulsive force to the foam forming agent. Such one component systems are typically and preferably packaged in a container, such as an aerosol type can, and the blowing agent of the present invention thus preferably provides for expansion of the foam and/or the energy to transport the foam/foamable material from the package, and preferably both. Such systems and methods may comprise charging the package with a fully formulated system (preferably isocyanate/polyol system) and incorporating a gaseous blowing agent in accordance with the present invention into the package, preferably an aerosol type can.

[0072] Any of the methods well known in the art, such as those described in "Polyurethanes Chemistry and Technology," Volumes I and II, Saunders and Frisch, 1962, John Wiley and Sons, New York, NY, which is incorporated herein by reference, may be used or adapted for use in accordance with the foam forming embodiments of the present invention.

6. Use of TFMCB as a Nucleating Agent

[0073] An alternative feature of the present invention relates to a blowing agent composition in which the TFMCB can act as a nucleating agent. The invention therefore relates to blowing agent compositions, foaming compositions, and foams that use TFMCB as a nucleating agent in the formation of the foam. The TFMCB is used in combination with a blowing agent other than TFMCB, such as one or more of HFC-152a, HFC-245fa, HFC-134, HFC-134a, HFC-365mfc, propane, butane, pentane, cyclopentane, hexane, HFO-1234ze(E), HFO-1234yf, HFO-1336mzz(E), HFO-1336mzz(Z), HFO-1233zd(E), HFO-1233zd(Z), HFO-1224yd(E), HFO-1224yd(Z), C1-C4 alcohol, *trans*-dichloroethylene (*trans*-DCE), methyl formate, C1 – C4 aldehydes, C3 – C4 ketones, C2 – C4 ethers, diethers, water, CO_2, and combinations thereof.

[0074] The blowing agent composition including TFMCB as a nucleating agent may comprise the TFMCB in an amount as low as about 0.5, about 1 wt.%, about 1.5 wt.%, about 2 wt.%, about 2.5 wt.%, about 3 wt.%, or about 3.5 wt.%, or as high as about 4 wt.%, about 4.5 wt.%, about 5 wt.%, about 5.5 wt.%, about 6 wt.%, about 6.5 wt.% or about 7 wt.%, or any value between any two of the forgoing values, such as about 0.5 wt.% to about 7 wt.%, about 1 wt.% to about 6.5 wt. about 1.5 wt.% to about 6 wt.%, about 2 wt.% to about 5.5 wt.%, about 2.5 wt.% to about 5 wt.%, about 3 wt.% to about 4.5 wt.%, about 3.5 wt.% to about 4 wt.%, about 2 wt.% to about 4 wt.%, or about 1 wt.% to about 3.5 wt.%, for example. Preferably, the blowing agent composition including TFMCB as a nucleating agent includes TFMCB from about 1 wt.% to about 7 wt.%. More preferably, the blowing agent composition including TFMCB as a nucleating agent includes TFMCB from about 2 wt.% to about 6 wt.%. Most preferably, the blowing agent composition including TFMCB as a nucleating agent includes TFMCB from about 3 wt.% to about 5 wt.%.

[0075] It has been surprisingly found that when TFMCB is used in a blowing agent composition at concentrations of 7 wt.% or lower, it functions as a nucleating agent. The resulting foams show a reduction in thermal conductivity when TFMCB is used as a nucleating agent.

[0076] The invention further relates to the use of TFMCB as a nucleating agent in the formation of a thermoplastic foam.

[0077] The thermoplastic foam is preferably polyethylene (PE), polypropylene (PP), polystyrene (PS) or polyethyleneterepthalate (PET). Preferably, the thermoplastic foam is an extruded thermoplastic foam. More particularly the foam is an extruded polystyrene foam.

[0078] When the foam is a thermoplastic foam, the blowing agent of the present invention preferably comprises one or more of CO2, HFC-152a, HFC-245fa, HFC-134, HFC-134a, butane, isobutane, HFO-1234ze(E), HFO-1234yf, HFO-1336mzz(E), HFO-1336mzz(Z), HFO-1233zd(E), HFO-1233zd(Z), HFO-1224yd(E), HFO-1224yd(Z), ethanol, dimethylether, acetone, methyl formate, cyclopentane and methylal.

[0079] The invention further relates to the use of TFMCB as a nucleating agent in the formation of a thermoset foam. The thermoset foam is preferably a polyisocyanate, polyurethane or phenolic foam.

[0080] When the foam is a thermoset foam, the blowing agent of the present invention preferably comprises one or more of water, CO2, methyl formate, methylal, HFO-1234ze(E), HFO-1234yf, HFO-1336mzz(E), HFO-1336mzz(Z), HFO-1233zd(E), HFO-1233zd(Z), HFO-1224yd(E), HFO-1224yd(Z), HFC-152a, formic acid, n-pentane, isopentane, cyclopentane, *trans*-1,2-dichloroethylene, HFC-245fa, HFC-365mfc, HFC-134a and HFC-134a.

[0081] When the TFMCB is present as a nucleating agent in a blowing agent composition to produce a foam, it is preferably present in the foam in an amount as low as about 0.1, about 0.2 wt.%, about 0.3 wt.%, about 0.4 wt.%, about 0.6 wt.%, about 0.8 wt.%, or about 1 wt.%, or as high as about 1.2 wt.%, about 1.4 wt.%, about 1.6 wt.%, about 1.8 wt.%, about 2 wt.%, about 2.5 wt.% or about 3 wt.%, or any value between any two of the forgoing values, such as about 0.1 wt.% to about 3 wt.%, about 0.2 wt.% to about 2.5 wt. about 0.3 wt.% to about 2 wt.%, about 0.4 wt.% to about 1.8 wt.%, about 0.6 wt.% to about 1.6 wt.%, about 0.8 wt.% to about 1.4 wt.%, about 1 wt.% to about 1.2 wt.%, about 0.1 wt. to about 1 wt.%, about 1 wt.% to about 2 wt.%, or about 1.2 wt.% to about 2.5 wt.%, for example. Preferably, the foam produced includes TFMCB from about 0.4 wt.% to about 2.5 wt.%. More preferably, the foam produced includes TFMCB from about 0.6 wt.% to about 2 wt.%. Most preferably, the foam produced includes TFMCB from about 0.8 wt.% to about 1.2 wt.%. All weight percentages are of the total foam weight.

EXAMPLES

EXAMPLE 1

Impact of TFMCB on Polyurethane Foam Blown with Cyclopentane

[0082] A polyurethane foam was prepared from the following composition: Stepanpol PS 2352 polyol (100 pphp), Lupranate M 20 polymeric isocyanate (173 pphp), NIAX Silicone L-6900 surfactant (2 pphp), Dabco K15 (2 pphp), Polycat 8 (0.8 pphp), TCPP (15 pphp), and water (0.8 pphp). Different dosages of TFMCB were studied regarding its impact on the thermal conductivity of the polyurethane foam blown with cyclopentane (cP). The compositions including TFMCB as a blowing agent and nucleating agent are shown in Table 1.

[0083] The polyol preblend was allowed to react with an isocyanate to produce a polyurethane foam. The foam sample was allowed to cure for 24hrs before cutting. The thermal conductivity value was recorded using the LaserComp FOX50 Heat Flow Meter on a 12"X12"X1" sample.

Table 1

Polyurethane foam properties blown with TFMCB and Cyclopentane (cP)

Blowing Agent/Nucleating Agent Composition				**Thermal Conductivity (mW/mK) @ Specified Temperature**		
Cyclopentane (pphp)	**TFMCB (pphp)**	**TFMCB (wt %)**	**Density (pcf)**	**50 °F**	**75 °F**	**130 °F**

17.76	0	0	2.01	23.31	23.8	27.6
17.32	1.13	6.1	2.09	22.10	22.55	26.24
16.87	2.26	11.8	2.18	22.54	22.98	26.75
15.99	4.52	22.0	2.04	23.18	23.22	27.04
14.21	9.03	38.9	2.13	22.03	22.04	25.88

[0084] As seen in Table 1, polyurethane foam samples blown with TFMCB and cP surprisingly show a decreased thermal conductivity below about 7 wt.% TFMCB as the TFMCB functions as a nucleating agent. Above about 7 wt.%, the thermal conductivity increases as TFMCB functions as more of a blowing agent, replacing the higher thermal conductivity cP. This effect is found at all temperatures and indicates better thermal insulation properties of the foam with TFMCB used as a nucleating agent.

Example 2

Impact of TFMCB on polyurethane foam blown with R-245fa

[0085] A polyurethane foam was prepared from the following composition: Stepanpol PS 2352 polyol (100 pphp), Lupranate M 20 polymeric isocyanate (173 pphp), NIAX Silicone L-6900 surfactant (2 pphp), Dabco K15 (2 pphp), Polycat 8 (0.8 pphp), TCPP (15 pphp), and water (0.8 pphp). Different dosages of TFMCB were studied regarding its impact on the thermal conductivity of the polyurethane foam blown with R245fa. The compositions including TFMCB as a blowing agent and nucleating agent are shown in Table 2.

[0086] The polyol preblend was allowed to react with an isocyanate to produce a polyurethane foam. The foam sample was allowed to cure for 24hrs before cutting. The thermal conductivity value was recorded using the LaserComp FOX50 Heat Flow Meter on a 12”X12”X1” sample.

Table 2

Polyurethane foam properties blown with TFMCB and R245fa

Blowing Agent/Nucleating Agent Composition				**Thermal Conductivity (mW/mK) @ Specified Temperature**		
R245fa (pphp)	**TFMCB (pphp)**	**TFMCB (wt %)**	**Density (pcf)**	**50 °F**	**75 °F**	**130 °F**
34.00	0	0	2.03	19.3	21.07	25.14
32.30	**2.26**	**6.5**	**2.13**	**18.95**	**20.55**	**24.72**
30.60	4.52	12.9	2.08	19.79	21.06	23.95

27.20	9.03	24.9	2.31	20.27	21.14	24.17
23.80	13.55	36.3	2.17	20.27	21.12	24.59

[0087] As seen in Table 2, polyurethane foam samples blown with TFMCB and R-245fa surprisingly show a decreased thermal conductivity below about 7 wt.% TFMCB as the TFMCB functions as a nucleating agent. Above about 7 wt.%, the thermal conductivity increases as TFMCB functions as more of a blowing agent, replacing the R245fa. The nucleating effect is not as dramatic as in Example 2 due to the lower thermal conductivity of the R245fa, compared to cP. This effect is found at 50°F and 75°F and indicates better thermal insulation properties of the foam with TFMCB used as a nucleating agent.

Example 3

Impact of TFMCB on polyurethane foam blown with R-1233zd(E) (Solstice® LBA)

[0088] A polyurethane foam was prepared from the following composition: Stepanpol PS 2352 polyol (100 °p), Lupranate M 20 polymeric isocyanate (173 pphp), NIAX Silicone L-6900 surfactant (2 pphp), Dabco K15 (2 pphp), Polycat 8 (0.8 pphp), TCPP (15 pphp), and water (0.8 pphp). Different dosages of TFMCB were studied regarding its impact on the thermal conductivity of the polyurethane foam blown with R-1233zd(E). The compositions including TFMCB as a blowing agent and nucleating agent are shown in Table 3.

[0089] The polyol preblend was allowed to react with an isocyanate to produce a polyurethane foam. The foam sample was allowed to cure for 24hrs before cutting. The thermal conductivity value was recorded using the LaserComp FOX50 Heat Flow Meter on a 12”X12”X1” sample.

Table 3

Polyurethane foam properties blown with TFMCB and R1233zd(E)

Blowing Agent/Nucleating Agent Composition				**Thermal Conductivity (mW/mK) @ Specified Temperature**		
R1233zd(E) (pphp)	**TFMCB (pphp)**	**TFMCB (wt %)**	**Density (pcf)**	**50 °F**	**75 °F**	**130 °F**
33.00	0	0	2.01	18.85	20.42	24.22
32.18	**1.13**	**3.4**	**2.09**	**19.08**	**20.65**	**24.46**
31.35	**2.26**	**6.7**	**2.18**	**18.48**	**19.89**	**23.60**
29.70	4.52	13.2	2.04	18.66	19.95	23.70
26.40	9.04	25.5	2.13	19.41	20.39	23.95

[0090] As seen in Table 3, polyurethane foam samples blown with TFMCB and R-1233zd(E) still show the surprising effect of decreased thermal conductivity below about 7 wt.% TFMCB as the TFMCB functions as a nucleating agent. The nucleating effect is not as dramatic as in Example 2 due to the lower thermal conductivity of the R-1233zd(E), compared to cP. This effect is found at all temperatures and indicates better thermal insulation properties of the foam with TFMCB used as a nucleating agent.

Example 4

Impact of TFMCB on polyurethane foam blown with HFO-1336mzz(Z)

[0091] A polyurethane foam was prepared from the following composition: Stepanpol PS 2352 polyol (100 °p), Lupranate M 20 polymeric isocyanate (173 pphp), NIAX Silicone L-6900 surfactant (2 pphp), Dabco K15 (2 pphp), Polycat 8 (0.8 pphp), TCPP (15 pphp), and water (0.8 pphp). Different dosages of TFMCB were studied regarding its impact on the thermal conductivity of the polyurethane foam blown with HFO-1336mzz(Z). The compositions including TFMCB as a blowing agent and nucleating agent are shown in Table 4.

Table 4

Polyurethane foam properties blown with TFMCB and HFO-1336mzz(Z)

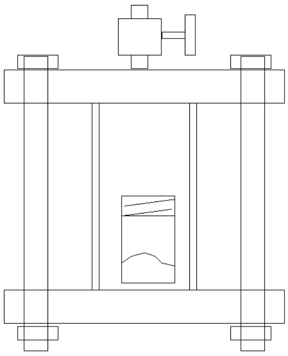
Blowing Agent/Nucleating Agent Composition				**Thermal Conductivity (mW/mK) @ Specified Temperature**		
1336mzz(Z)) (pphp)	**TFMCB (pphp)**	**TFMCB (wt %)**	**Density (pcf)**	**50 °F**	**75 °F**	**130 °F**
41.63	0	0	2.26	21.37	20.24	23.26
40.59	**1.13**	**2.7**	**2.34**	**21.15**	**19.85**	**22.98**
39.55	**2.26**	**5.4**	**2.32**	**21.26**	**20.02**	**23.07**
37.47	4.52	10.8	2.33	21.75	20.43	23.17
33.30	9.04	21.4	2.31	22.47	21.31	23.65

[0092] As seen in Table 4, polyurethane foam samples blown with TFMCB and HFO-1336mzz(Z) still show the surprising effect of decreased thermal conductivity below about 7 wt.% TFMCB as the TFMCB functions as a nucleating agent. This effect is found at all temperatures and indicates better thermal insulation properties of the foam with TFMCB used as a nucleating agent.

Example 5

[0093] This example illustrates the use of blowing agent compositions in accordance with the present invention in the production of polystyrene foam.

[0094] A testing apparatus and protocol has been established as an aid to determining whether a specific blowing agent and polymer are capable of producing a foam and the quality of the foam. Ground polymer (Dow Polystyrene 685D) and blowing agent are combined in a vessel. A sketch of the vessel is illustrated below. The vessel volume is 200 cm^3 and it is made from two pipe flanges and a section of 2-inch diameter schedule 40 stainless steel pipe 4 inches long. The vessel is placed in an oven, with temperature set at from about 190ºF to about 285ºF, preferably for polystyrene at 265ºF, and remains there until temperature equilibrium is reached.



[0095] The pressure in the vessel is then released, quickly producing a foamed polymer. The blowing agent plasticizes the polymer as it dissolves into it. The resulting density of the foams thus produced using this method are given in Tables 1-4 above. The data show that foam polystyrene is obtainable in accordance with the present invention.

Example 6

Polystyrene Foam

[0096] This example demonstrates the performance of TFMCB a blowing agent for polystyrene foam formed in a twin screw type extruder. The apparatus employed in this example is a Leistritz twin screw extruder having the following characteristics:

- 30 mm co-rotating screws

- L:D Ratio = 40:1

[0097] The extruder is divided into 10 sections, each representing a L:D of 4:1. The polystyrene resin was introduced into the first section, the blowing agent was introduced into the sixth section, with the extrudate exiting the tenth section. The extruder operated primarily as a melt /mixing extruder. A subsequent cooling extruder is connected in tandem, for which the design characteristics were:

- Leistritz twin screw extruder
- 40 mm co-rotating screws
- L:D Ratio = 40:1
- Die: 5.0 mm circular

[0098] Polystyrene resin, namely Nova Chemical – general extrusion grade polystyrene, identified as Nova 1600, is feed to the extruder under the conditions indicated above. The resin has a recommended melt temperature of 375 °F – 525 °F. The pressure of the extruder at the die is about 1320 pounds per square inch (psi), and the temperature at the die is about 115 °C.

[0099] A blowing agent consisting essentially of TFMCB is added to the extruder at the location indicated above, with about 0.5% by weight of talc being included, on the basis of the total blowing agent, as a nucleating agent. The foams, of approximately 30 millimeters diameter, are visually of very good quality, very fine cell size, with no visible or apparent blow holes or voids.

Example 7
Polystyrene Foam

[00100] This procedure of Example 6 is repeated except that the nucleating agent is omitted. The foams' density was in the range of 0.1 grams per cubic centimeter, and the cell size diameter is about 400 nm. The foams, of approximately 30 millimeters diameter, are visually of very good quality, fine cell structure, with no visible or apparent voids.

Example 8
Polyurethane Foam Compressive Strength

[00101] This example demonstrates the performance of TFMCB, used in combination with hydrocarbon co-blowing agents, and in particular the utility of compositions comprising TFMCB and cyclopentane co-blowing agents in compressive strength performance of polyurethane foams.

[00102] A commercially available, refrigeration appliance-type polyurethane foam formulation (foam forming agent) is provided. The polyol blend consisted of commercial polyol(s), catalyst(s), and surfactant(s). Standard commercial polyurethane processing equipment is used for the foam forming process. A blowing agent combination was formed comprising TFMCB in a concentration of approximately 60 mole percent, and cyclopentane in a concentration of approximately 40 mole percent of the total blowing agent. This example illustrates the physical property performance of combinations of TFMCB in combination with cyclopentane co-blowing agent.

Example 9

Polyurethane Foam K-Factors

[00103] A polyurethane foam is prepared and is adapted for use as a commercial "appliance type" polyurethane formulation. The same foam formulation described in Example 1 is used in connection with the same standard commercial polyurethane processing equipment is used in the foam forming process. Several systems are prepared, with each system using identical components, systems, and equipment, with the exception of the blowing agent. In addition to the blowing agent in accordance with the present invention, HFC-134a, HFC-245fa, and cyclopentane are each also tested as the blowing agent. In each system, the blowing agent is added in substantially the same molar concentration into the polyol blend. The polyol blend consists of commercial polyol(s), catalyst(s), and surfactant(s). The foams are prepared in accordance with standard commercial manufacturing operations, for example a commercial operation for making foam for refrigeration applications.

Example 10

Polystyrene Foam

[00104] This example demonstrates the performance of a blowing agent composition including TFMCB as a nucleating agent and a blowing agent other than TFMCB for polystyrene foam formed in a twin screw type extruder. The apparatus is a Leistritz twin screw extruder having the following characteristics:

- 30 mm co-rotating screws
- L:D Ratio = 40:1

[00105] The extruder is divided into 10 sections, each representing a L:D of 4:1. The polystyrene resin is introduced into the first section, the blowing agent composition is introduced into the sixth section, with the extrudate exiting the tenth section. The extruder operates primarily as a melt /mixing extruder. A subsequent cooling extruder is connected in tandem, for which the design characteristics are:

- Leistritz twin screw extruder
- 40 mm co-rotating screws

- L:D Ratio = 40:1
- Die: 5.0 mm circular

[00106] Polystyrene resin, namely Nova Chemical – general extrusion grade polystyrene, identified as Nova 1600, is fed to the extruder under the conditions indicated above. The resin is at a recommended melt temperature of 375 °F – 525 °F. The pressure of the extruder at the die is about 1320 pounds per square inch (psi), and the temperature at the die is about 115 °C.

[00107] A blowing agent composition consisting essentially of TFMCB as a nucleating agent and a blowing agent other than TFMCB is added to the extruder at the location indicated above. The foams of approximately 30 millimeters diameter are produced.

Example 11

Polyurethane Foam Compressive Strength

[00108] This example demonstrates the performance of TFMCB as a nucleating agent, used in combination with hydrocarbon blowing agents, and in particular the utility of compositions comprising TFMCB as a nucleating agent and cyclopentane as a blowing agent in producing polyurethane foams and the compressive strength performance of such polyurethane foams.

[00109] A commercially available, refrigeration appliance-type polyurethane foam formulation (foam forming agent) is provided. The polyol blend consists of commercial polyol(s), catalyst(s), and surfactant(s). Standard commercial polyurethane processing equipment is used for the foam forming process. A blowing agent composition is formed comprising TFMCB in a concentration of approximately 6.5 wt.% and cyclopentane as the blowing agent. This example illustrates the physical property performance of blowing agent compositions including TFMCB as a nucleating agent and cyclopentane as blowing agent.

Example 12

Polyurethane Foam K-Factors

[00110] A polyurethane foam is prepared and is adapted for use as a commercial “appliance type” polyurethane formulation. The same foam formulation described in Example 1 is used in connection with the same standard commercial polyurethane processing equipment is used in the foam forming process. Several systems are prepared, with each system using identical components, systems, and equipment, with the exception of the blowing agent composition. In addition to blowing agent compositions including TFMCB as a nucleating agent and a blowing agent including cyclopentane, HFC-245fa, R-1233zd(E), or HFO-1336mzz(Z), in accordance with the present invention, cyclopentane, HFC-245fa, R-1233zd(E), or HFO-1336mzz(Z) are each also tested as the blowing agent without TFMCB as a nucleating agent. In each system, the blowing agent composition is added in substantially the same molar concentration into the polyol blend. The polyol blend consists of commercial polyol(s), catalyst(s), and surfactant(s). The foams are prepared in accordance with standard commercial manufacturing operations, for example a commercial operation for making foam for refrigeration applications.

ASPECTS

[00111] The invention will now be illustrated by reference to the following numbered embodiments. The subject matter of the numbered embodiments may be additionally combined with subject matter from the description or from one or more of the claims.

[00112] Aspect 1 is a blowing agent composition comprising a blowing agent and a nucleating agent. The nucleating agent includes 1,2,2-trifluoro-1-trifluoromethylcyclobutane (TFMCB). The TFMCB is present in the blowing agent composition in an amount from about 0.5 wt.% to about 7 wt.% of the blowing agent composition.

[00113] Aspect 2 is the blowing agent composition of Aspect 1, wherein the blowing agent comprises HFC-152a, HFC-245fa, HFC-134, HFC-134a, HFC-365mfc, propane, butane, pentane, cyclopentane, hexane, HFO-1234ze(E), HFO-1234yf, HFO-1336mzz(E), HFO-1336mzz(Z), HFO-1233zd(E), HFO-1233zd(Z), HFO-1224yd(E), HFO-1224yd(Z), C1-C4 alcohol, *trans*-dichloroethylene (*trans*-DCE), methyl formate, C1 – C4 aldehydes, C3 – C4 ketones, C2 – C4 ethers, diethers, water, CO2, and combinations thereof.

[00114] Aspect 3 is the blowing agent composition of Aspect 2, wherein the blowing agent comprises cyclopentane, HFC-245fa, R-1233zd(E), HFO-1336mzz(Z), or combinations thereof.

[00115] Aspect 4 is the blowing agent composition of Aspect 3, wherein the blowing agent consists of cyclopentane

[00116] Aspect 5 is the blowing agent composition of Aspect 3, wherein the blowing agent consists of HFC-245fa.

[00117] Aspect 6 is the blowing agent composition of Aspect 3, wherein the blowing agent consists of R-1233zd(E).

[00118] Aspect 7 is the blowing agent composition of Aspect 3, wherein the blowing agent consists of HFO-1336mzz(Z).

[00119] Aspect 8 is the blowing agent composition of any of Aspects 1 to 7, further comprising at least one adjuvant selected from the group consisting of: surfactant(s), polymer modifier(s), toughening agent(s), colorant(s), dye(s), solubility enhancer(s), rheology modifier(s), plasticizing agent(s), flammability suppressant(s), antibacterial agent(s), viscosity reduction modifier(s), filler(s), vapor pressure modifier(s), catalyst(s) and combination of any two or more of these

[00120] Aspect 9 is the blowing agent composition of any of Aspects 1 to 8, wherein the TFMCB present in the composition in an amount from about 1 wt.% to about 7 wt.% of the blowing agent composition.

[00121] Aspect 10 is the blowing agent composition of any of Aspects 1 to 8, wherein the TFMCB present in the composition in an amount from about 2 wt.% to about 6 wt.% of the blowing agent composition.

[00122] Aspect 11 is the blowing agent composition of any of Aspects 1 to 8, wherein the TFMCB present in the composition in an amount from about 3 wt.% to about 5 wt.% of the blowing agent composition

[00123] Aspect 12 is the use of the blowing agent composition of any of Aspects 1 to 11 in the production of a foam.

[00124] Aspect 13 is the use of the blowing agent composition of any of Aspects 1 to 11 in the production of a thermoplastic foam.

[00125] Aspect 14 it the use of Aspect 13 where the thermoplastic foam is polyethylene (PE), polypropylene (PP), polystyrene (PS) or polyethyleneterepthalate (PET).

[00126] Aspect 15 is the use of any of Aspects 13 or 14 where the thermoplastic foam is an extruded thermoplastic foam.

[00127] Aspect 16 is the use of any of Aspects 13 or 14 where the thermoplastic foam is an extruded polystyrene foam.

[00128] Aspect 17 is the use of any of Aspects 13 to 16 where the blowing agent comprises HFC-152a, HFC-245fa, HFC-134, HFC-134a, HFC-365mfc, propane, butane, pentane, cyclopentane, hexane, HFO-1234ze(E), HFO-1234yf, HFO-1336mzz(E), HFO-1336mzz(Z), HFO-1233zd(E), HFO-1233zd(Z), HFO-1224yd(E), HFO-1224yd(Z), C1-C4 alcohol, *trans*-dichloroethylene (*trans*-DCE), methyl formate, C1 – C4 aldehydes, C3 – C4 ketones, C2 – C4 ethers, diethers, water, CO2, and combinations thereof.

[00129] Aspect 18 is the use of the blowing agent composition of any of Aspects 1 to 17 in the production of a thermoset foam.

[00130] Aspect 19 is the use of Aspect 18 where the thermoset foam is a polyisocyanate, polyurethane or phenolic foam.

[00131] Aspect 20 is a foamable composition comprising a foam forming agent and a blowing agent composition. The blowing agent comprises a blowing agent and a nucleating agent. The nucleating agent includes 1,2,2-trifluoro-1-trifluoromethylcyclobutane (TFMCB). The TFMCB is present in the blowing agent composition in an amount from about 0.5 wt.% to about 7 wt.% of the blowing agent composition.

[00132] Aspect 21 is the foamable composition of Aspect 20, wherein the foam forming agent comprises at least one thermoset foam component.

[00133] Aspect 22 is the foamable composition of Aspect 21, wherein the at least one thermoset component is capable of forming polyurethane foam.

[00134] Aspect 23 is the foamable composition of Aspect 20, wherein the foam forming agent comprises at least one thermoplastic foam component

[00135] Aspect 24 is the foamable composition of Aspect 23, wherein the at least one thermoplastic foam component is selected from the group consisting of polystyrene, ethylene homopolymers, polypropylene, polyethyleneterepthalate (PET) and combinations of these

[00136] Aspect 25 is the foamable composition of any of Aspects 20 to 24, wherein the blowing agent comprises HFC-152a, HFC-245fa, HFC-134, HFC-134a, HFC-365mfc, propane, butane, pentane, cyclopentane, hexane, HFO-1234ze(E), HFO-1234yf, HFO-1336mzz(E), HFO-1336mzz(Z), HFO-1233zd(E), HFO-1233zd(Z), HFO-1224yd(E), HFO-1224yd(Z), C1-C4 alcohol, *trans*-dichloroethylene (*trans*-DCE), methyl formate, C1 – C4 aldehydes, C3 – C4 ketones, C2 – C4 ethers, diethers, water, CO2, and combinations thereof

[00137] Aspect 26 is the foamable composition of Aspect 25, wherein the blowing agent comprises cyclopentane, HFC-245fa, R-1233zd(E), HFO-1336mzz(Z), or combinations thereof.

[00138] Aspect 27 is the foamable composition of Aspect 26, wherein the blowing agent consists of cyclopentane.

[00139] Aspect 28 is the foamable composition of Aspect 26, wherein the blowing agent consists of HFC-245fa.

[00140] Aspect 29 is the foamable composition of Aspect 26, wherein the blowing agent consist of R-1233zd(E).

[00141] Aspect 30 is the foamable composition of Aspect 256 wherein the blowing agent consist of HFO-1336mzz(Z)

[00142] Aspect 31 is a foam comprising a plurality of polymeric cells and a composition contained in at least one of the cells. The composition comprises a blowing agent and a nucleating agent. The nucleating agent includes 1,2,2-trifluoro-1-trifluoromethylcyclobutane (TFMCB). The TFMCB is present in the cell in an amount from about 0.1 wt.% to about 3 wt.% of the composition.

[00143] Aspect 32 is the foam composition of Aspect 21, wherein the TFMCB is present in the cell in an amount from about 0.4 wt.% to about 2.5 wt.% of the composition.

[00144] Aspect 33 is the foam composition of Aspect 21, wherein the TFMCB is present in the cell in an amount from about 0.6 wt.% to about 2 wt.% of the composition.

[00145] Aspect 34 is the foam composition of Aspect 21, wherein the TFMCB is present in the cell in an amount from about 0.8 wt.% to about 1.2 wt.% of the composition.

[00146] Aspect 35 is the foam of any of Aspects 31 to 34 in the form of a rigid foam.

[00147] Aspect 36 is the foam of any of Aspects 31 to 34 in the form of a flexible foam.

[00148] Aspect 37 is the foam of any of Aspects 31 to 34 in the form of an integral skin foam.

[00149] Aspect 38 is the foam of any of Aspects 31 to 37 in the form of an open cell foam.

[00150] Aspect 39 is the foam of any of Aspects 31 to 37 in the form of a closed cell foam.

[00151] Aspect 40 is the foam of any of Aspects 31 to 39 which is a block, a slab, a laminate, a panel, such as a pour-in-place panel, a spray applied foam, a froth, and the like.

[00152] Aspect 41 is the foam of any of Aspects 31-39 which is an appliance foam.

[00153] Aspect 42 is the foam of Aspect 41 which is a refrigerator foam, freezer foam, refrigerator/freezer foam, panel foam, and foam for other cold or cryogenic manufacturing applications.

[00154] Aspect 43 is the foam of any of Aspects 31-42 which is an extruded thermoplastic foam.

[00155] Aspect 44 is the foam of Aspects 31-42 which is an extruded polystyrene foam.

[00156] Aspect 45 is a refrigerator comprising the foam of any of Aspects 31-44.

[00157] Aspect 46 is a freezer comprising the foam of any of Aspects 31-44.

[00158] Aspect 47 is a method of forming a foam of any of Aspects 31-44 comprising introducing a blowing agent composition of Aspects 1 to 11 into a foam forming agent and then subjecting the foam forming agent to conditions effective to cause foaming.

[00159] Aspect 48 is the method of Aspect 47, further comprising providing the foam forming agent, wherein providing the foam forming agent comprises mixing a polyol and an isocyanate together, and reacting the polyol and the isocyanate together.

WHAT IS CLAIMED IS:

1. A blowing agent composition comprising:

a blowing agent; and

a nucleating agent, the nucleating agent including 1,2,2-trifluoro-1-trifluoromethylcyclobutane (TFMCB), the TFMCB present in the blowing agent composition in an amount from about 0.5 wt.% to about 7 wt.% of the blowing agent composition.

2. The blowing agent composition of claim 1, wherein the blowing agent comprises HFC-152a, HFC-245fa, HFC-134, HFC-134a, HFC-365mfc, propane, butane, pentane, cyclopentane, hexane, HFO-1234ze(E), HFO-1234yf, HFO-1336mzz(E), HFO-1336mzz(Z), HFO-1233zd(E), HFO-1233zd(Z), HFO-1224yd(E), HFO-1224yd(Z), C1-C4 alcohol, *trans*-dichloroethylene (*trans*-DCE), methyl formate, C1 – C4 aldehydes, C3 – C4 ketones, C2 – C4 ethers, diethers, water, CO2, and combinations thereof.

3. The blowing agent composition of claim 2, wherein the blowing agent comprises cyclopentane, HFC-245fa, R-1233zd(E), HFO-1336mzz(Z), or combinations thereof.

4. The blowing agent composition of claim 3, wherein the blowing agent consists of cyclopentane.

5. The blowing agent composition of claim 1, further comprising at least one adjuvant selected from the group consisting of: surfactant(s), polymer modifier(s), toughening agent(s), colorant(s), dye(s), solubility enhancer(s), rheology modifier(s), plasticizing agent(s), flammability suppressant(s), antibacterial agent(s), viscosity reduction modifier(s), filler(s), vapor pressure modifier(s), catalyst(s) and combination of any two or more of these.

6. The blowing agent composition of claim 1, wherein the TFMCB present in the composition in an amount from about 1 wt.% to about 7 wt.% of the blowing agent composition.

7. The blowing agent composition of claim 1, wherein the TFMCB present in the composition in an amount from about 2 wt.% to about 6 wt.% of the blowing agent composition.

8. A foamable composition comprising:

a foam forming agent; and

the blowing agent composition of any of claims 1-7.

9. A foam comprising:

a plurality of polymeric cells; and

a composition contained in at least one of the cells, the composition comprising:

a blowing agent; and

a nucleating agent, the nucleating agent including 1,2,2-trifluoro-1-trifluoromethylcyclobutane (TFMCB), the TFMCB present in the cell in an amount from about 0.1 wt.% to about 3 wt.% of the composition.

10. The foam of claim 9 wherein the blowing agent comprises HFC-152a, HFC-245fa, HFC-134, HFC-134a, HFC-365mfc, propane, butane, pentane, cyclopentane, hexane, HFO-1234ze(E), HFO-1234yf, HFO-1336mzz(E), HFO-1336mzz(Z), HFO-1233zd(E), HFO-1233zd(Z), HFO-1224yd(E), HFO-1224yd(Z), C1-C4 alcohol, *trans*-dichloroethylene (*trans*-DCE), methyl formate, C1 – C4 aldehydes, C3 – C4 ketones, C2 – C4 ethers, diethers, water, CO2, and combinations thereof.