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CA 2875315 C 2017/10/24

(11)(21) **2 875 315**

(12) **BREVET CANADIEN**
CANADIAN PATENT

(13) **C**

(22) **Date de dépôt/Filing Date:** 2008/02/20
(41) **Mise à la disp. pub./Open to Public Insp.:** 2009/01/08
(45) **Date de délivrance/Issue Date:** 2017/10/24
(62) **Demande originale/Original Application:** 2 691 584
(30) **Priorité/Priority:** 2007/07/05 (US11/773,958)

(51) **Cl.Int./Int.Cl. C08J 9/14** (2006.01)
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(54) **Titre : COMPOSITIONS DE TETRAFLUOROPROPENE ET D'HYDROCARBURES**
(54) **Title: COMPOSITIONS OF TETRAFLUOROPROPENE AND HYDROCARBONS**

(57) Abrégé/Abstract:

Provided are azeotrope-like compositions comprising tetrafluoropropene and one or more selected hydrocarbons and uses thereof, including use in blowing agent and foamable compositions, having a low ozone depletion potential.

ABSTRACT

Provided are azeotrope-like compositions comprising tetrafluoropropene and one or more selected hydrocarbons and uses thereof, including use in blowing agent and foamable compositions, having a low ozone depletion potential.

**COMPOSITIONS OF
TETRAFLUOROPROPENE AND HYDROCARBONS**

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FIELD OF INVENTION

The present invention relates generally to compositions comprising 1,3,3,3-tetrafluoropropene. More specifically, the present invention provides azeotrope-like compositions comprising 1,3,3,3-tetrafluoropropene, and particularly to trans-1,3,3,3-tetrafluoropropene and uses thereof.

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BACKGROUND

Fluorocarbon based fluids have found widespread use in industry in a number of applications, including as propellants, particularly, aerosol propellants. Such materials have also been used as refrigerants, blowing agents, heat transfer media, and gaseous dielectrics. Because of the suspected environmental problems associated with the use of some of these fluids, including the relatively high global warming potentials associated therewith, it is desirable to use fluids having low or even zero ozone depletion potential, such as hydrofluorocarbons ("HFCs"). Thus, the use of fluids that do not contain chlorofluorocarbons ("CFCs") or hydrochlorofluorocarbons ("HCFCs") is desirable. Furthermore, some HFC fluids may have relatively high global warming potentials associated therewith, and it is desirable to use hydrofluorocarbon or other fluorinated fluids having global warming potentials as low as possible while maintaining the desired performance properties. The properties of

stability and relatively low toxicity are desired in many applications. Additionally, low or non-flammability and the use of single component fluids or azeotrope-like mixtures, which do not substantially fractionate on boiling and evaporation, is desirable in certain applications.

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The identification of new, environmentally-safe, non-fractionating mixtures is complicated due to the fact that azeotrope formation is not readily predictable.

DESCRIPTION OF PREFERRED EMBODIMENTS

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The present inventors have developed several compositions that help to satisfy the continuing need for alternatives to CFCs and HCFCs. According to certain embodiments, the present invention provides compositions, and preferably azeotrope-like compositions, comprising, or consisting essentially of, 1,3,3,3-tetrafluoropropene ("HFO-1234ze"), preferably trans-1,1,1,3-tetrafluoropropene ("transHFO-1234ze") and at least one compound selected from the group consisting of propane, isobutane, n-butane, 2-methyl butane and combinations of two or more of these. Thus, preferred aspects of the present invention overcome at least some of the aforementioned shortcomings by providing azeotrope-like compositions that have, in preferred embodiments, desirably low global warming potentials. In addition, the preferred compounds to be used in combination with HFO-1234 to form the azeotropic or azeotrope-like compositions are hydrocarbons (hereinafter sometimes referred to for convenience as "HCs") and therefore the present compositions are capable of being used with good effect while being substantially free of CFCs and HCFCs. Moreover, the present azeotrope-like compositions generally exhibit relatively constant boiling point and vapor pressure characteristics.

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The preferred compositions of the invention tend to exhibit characteristics which make them particularly desirable for use in a number of applications, including as propellants, including particularly aerosol

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propellants. In other applications, the present compositions are useful as refrigerants in automotive air conditioning and heat pump systems, and in stationary air conditioning and refrigeration. Other applications in which the present composition are believed to be useful include, but are not limited to, blowing agents (such as are used in connection with foams, including thermoplastic foams), , and solvents for cleaning, flushing, deposition and extraction.

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In preferred embodiments, the present compositions tend to exhibit relatively low global warming potentials ("GWP"), preferably less than about 1200, more preferably less than about 1000, more preferably less than about 500, and even more preferably less than about 150. Certain embodiments of the present compositions tend also to have similar properties, for example similar or higher refrigeration capacity, than many conventional HFC materials. Accordingly, applicants have recognized that such compositions can be used to great advantage in a number of applications, including as replacements for CFCs such as dichlorodifluormethane (CFC-12), HCFCs, such as chlorodifluoromethane (HCFC-22), and HFCs, such as tetrafluoroethane (HFC-134a) and difluoromethane (HFC-152a), and combinations of HFCs and CFCs, such as the combination of CFC-12 and 1,1-difluorethane (HFC-152a) (the combination CFC-12:HFC-152a in a 73.8:26.2 mass ratio being known as R-500) in refrigerant, aerosol, and other applications.

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Additionally, applicants have recognized surprisingly that the preferred azeotrope-like compositions of the present invention exist and can be readily formed in view of the teachings contained herein. Accordingly, one aspect of the present invention provides methods of producing azeotrope-like compositions comprising the step of combining HFO-1234, preferably HFO-1234ze, and even more preferably transHFO-1234ze, and a compound selected from the group consisting of propane, n-butane, isobutane, and 2-methyl butane, and combinations of two or

more of these, in amounts effective to produce an azeotrope-like composition.

The term "HFO-1234" is used herein to refer to all tetrafluoropropenes. Among the tetrafluoropropenes are included HFO-1234yf and both cis- and trans-1, 3, 3, 3-tetrafluoropropene (HFO-1234ze). The term HFO-1234ze is used herein generically to refer to 1,3,3,3-tetrafluoropropene, independent of whether it is the cis- or trans-form. The terms "cisHFO-1234ze" and "transHFO-1234ze" are used herein to describe the cis- and trans- forms of 1,3,3,3-tetrafluoropropene respectively. The term "HFO-1234ze" therefore includes within its scope cisHFO-1234ze, transHFO-1234ze, and all combinations and mixtures of these.

Although the properties of cisHFO-1234ze and transHFO-1234ze differ in at least some respects, and while the present azeotrope-like compositions are based mainly on transHFO-1234ze, it is contemplated that the cisHFO-1234ze form may be present in certain embodiments in amounts which do not negate the essential nature of the azeotrope-like composition. Accordingly, it is to be understood that the terms "HFO-1234ze" and 1,3,3,3 -tetrafluoropropene refer to both stereo isomers, and the use of this term is intended to indicate that each of the cis-and trans-forms applies and/or is useful for the stated purpose unless otherwise indicated.

HFO-1234 compounds are known materials and are listed in Chemical Abstracts databases. The production of fluoropropenes such as CF₃CH=CH₂ by catalytic vapor phase fluorination of various saturated and unsaturated halogen-containing C₃ compounds is described in U.S. Patent Nos. 2,889,379; 4,798,818 and 4,465,786, EP 974,571 discloses the preparation of 1,3,3,3-tetrafluoropropene by contacting 1,1,1,3,3-pentafluoropropane (HFC-245fa) in the vapor phase with a chromium-based catalyst at elevated temperature, or in the liquid

phase with an alcoholic solution of KOH, NaOH, Ca(OH)2 or Mg(OH)2. In addition, methods for producing compounds in accordance with the present invention are described generally in connection with pending United States Patent Application entitled "Process for Producing Fluoropropenes", US Published Application Number 2004/0119047.

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In addition, applicants have recognized that the azeotrope-like compositions of the present invention exhibit properties that make them advantageous for use as, or in, numerous applications, including as propellants (particularly aerosol propellants), heat transfer compositions (including as refrigerants in automotive air conditioning and heat pump systems, and in stationary air conditioning, heat pump and refrigeration systems), blowing agents and carriers for sterilizing agents. Accordingly, yet other aspects of the present invention provide one or more azeotrope-like compositions of the present invention and methods associated with these and other uses.

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In certain highly preferred embodiments, the compositions of this invention are used as propellants in connection with or as part of sprayable compositions, either alone or in combination with known propellants. The propellant portions of such sprayable compositions comprise, more preferably consists essentially of, and, even more preferably consist of the compositions of the invention. The active ingredient to be sprayed together with inert ingredients, solvents, and other materials may also be present in the sprayable mixture. Preferably, the sprayable composition is an aerosol. Suitable active materials to be sprayed include, without limitation, cosmetic materials such as deodorants, perfumes, hair sprays, cleaning solvents, lubricants, as well as medicinal materials such as anti-asthma medications.

The present compositions find particular advantage in methods and systems involving aerosol compositions, particularly in medicinal compositions, cleaning composition, and other sprayable compositions.

Those of skill in the art will be readily able to adapt the present compositions for use in such applications without undue experimentation.

Azeotrope-like Compositions

5 As used herein, the term "azeotrope-like" is intended in its broad sense to include both compositions that are strictly azeotropic and compositions that behave like azeotropic mixtures. From fundamental principles, the thermodynamic state of a fluid is defined by pressure, temperature, liquid composition, and vapor composition. An azeotropic
10 mixture is a system of two or more components in which the liquid composition and vapor composition are equal at the stated pressure and temperature. In practice, this means that the components of an azeotropic mixture are constant-boiling and cannot be separated during a phase change.

15 Azeotrope-like compositions are constant boiling or essentially constant boiling. In other words, for azeotrope-like compositions, the composition of the vapor formed during boiling or evaporation is identical, or substantially identical, to the original liquid composition. Thus, with boiling or evaporation, the liquid composition changes, if at all, only to a
20 minimal or negligible extent. This is to be contrasted with non-azeotrope-like compositions in which, during boiling or evaporation, the liquid composition changes to a substantial degree. All azeotrope-like compositions of the invention within the indicated ranges as well as certain compositions outside these ranges are azeotrope-like.

25 The azeotrope-like compositions of the invention may include additional components that do not form new azeotrope-like systems, or additional components that are not in the first distillation cut. The first distillation cut is the first cut taken after the distillation column displays steady state operation under total reflux conditions. One way to determine
30 whether the addition of a component forms a new azeotrope-like system so as to be outside of this invention is to distill a sample of the composition

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with the component under conditions that would be expected to separate a non-azeotropic mixture into its separate components. If the mixture containing the additional component is non-azeotrope-like, the additional component will fractionate from the azeotrope-like components. If the mixture is azeotrope-like, some finite amount of a first distillation cut will be obtained that contains all of the mixture components that is constant boiling or behaves as a single substance.

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It follows from this that another characteristic of azeotrope-like compositions is that there is a range of compositions containing the same components in varying proportions that are azeotrope-like or constant boiling. All such compositions are intended to be covered by the terms "azeotrope-like" and "constant boiling". As an example, it is well known that at differing pressures, the composition of a given azeotrope will vary at least slightly, as does the boiling point of the composition. Thus, an azeotrope of A and B represents a unique type of relationship, but with a variable composition depending on temperature and/or pressure. It follows that, for azeotrope-like compositions, there is a range of compositions containing the same components in varying proportions that are azeotrope-like. All such compositions are intended to be covered by the term azeotrope-like as used herein.

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It is well-recognized in the art that it is not possible to predict the formation of azeotropes. (See, for example, U.S. Patent No. 5,648,017 (column 3, lines 64-65) and U.S. Patent No. 5,182,040 (column 3, lines 62-63). Applicants

have discovered unexpectedly that HFO-1234 and HCs, particularly the HCs described above, form azeotrope-like compositions.

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According to certain preferred embodiments, the azeotrope-like compositions of the present invention comprise, and preferably consist essentially of, effective amounts of HFO-1234 and the above-noted HCs. The term "effective amounts" as used herein with respect to azeotrope-like and azeotropic compositions refers to the amount of each component

which upon combination with the other component, results in the formation of an azeotrope-like composition of the present invention. With respect to compositions which are not necessarily azeotrope-like compositions, the term "effective amounts" means those amounts which will achieve the desired properties for the particular application. The compositions of the present invention, particularly the azeotrope-like or azeotropic compositions of the present invention, can be produced by combining effective amounts of HFO-1234 and a component, preferably in fluid form, selected from the group consisting of propane, n-butane, isobutane, 2-methyl butane and combinations of two or more of these. Any of a wide variety of methods known in the art for combining two or more components to form a composition can be adapted for use in the present methods to produce an azeotrope-like composition. For example, transHFO-1234ze and propane can be mixed, blended, or otherwise combined by hand and/or by machine, as part of a batch or continuous reaction and/or process, or via combinations of two or more such steps. In light of the disclosure herein, those of skill in the art will be readily able to prepare azeotrope-like compositions according to the present invention without undue experimentation.

Preferably, the present composition, particularly the azeotrope-like compositions, comprise, and preferably consist essentially of, from greater than zero to about 99 wt.% of of HFO-1234, preferably HFO-1234ze and even more preferably transHFO-1234ze, and from about 1 wt.% to less than 100 wt.% of one or more components selected from the group consisting propane, n-butane, isobutane, and 2-methyl butane. It will be appreciated by those skilled in the art that the production transHFO-1234ze will commonly result in product which includes a small proportion of compounds which are not transHFO-1234ze. For example, it would be common and expected for a product designated as transHFO-1234ze to include a minor percentage, for example about 0.5 wt. % up to about 1 wt. % of other components, including particularly cisHFO-1234ze and/or HFO-

1234yf. The term "consisting essentially of transHFO-1234ze" used herein is intended to generally include such compositions.

In certain embodiments, the present compositions comprise, and preferably consist essentially of, from about 5 wt.% to about 99 wt.% of HFO-1234, preferably HFO-1234ze and even more preferably transHFO-1234ze, and from about 10 wt.% to about 95 wt. % of one or more components selected from the group consisting propane, n-butane, isobutane, and 2-methyl butane. Other preferred compositions comprise, or consist essentially of, from about 20 wt.% to about 99 wt.% of HFO-1234, preferably HFO-1234ze and even more preferably transHFO-1234ze, and from about 1 wt.% to about 80 wt.% of one or more components selected from the group consisting n-butane and isobutane. Unless otherwise indicated, all weight percents reported herein are based on the total weight of the HFO-1234 and the one or more components selected from the indicated group in the composition.

According to certain preferred embodiments, the present transHFO-1234ze azeotrope-like compositions have a boiling point of from about -15°C to about -50°C, and even more preferably from about -18°C to about -45°C, at about 14.4 psia. In certain preferred embodiments, the present compositions have a boiling point of about -41°C ±2°C. In other preferred embodiments, the present compositions have a boiling point of about -20°C ±2°C. Additionally, in other preferred embodiments the present compositions have a boiling point of about -23°C ±1°C. Preferably, the HFO-1234 containing compositions of the present invention are substantially homogenous azeotrope-like compositions.

HFO-1234/Propane

Certain preferred embodiments of the present invention provide compositions, and preferably azeotrope-like compositions, comprising transHFO-1234ze and propane. Preferably, the novel azeotrope-like compositions of the present invention comprise effective amounts of

transHFO-1234ze and propane. These embodiments preferably provide azeotrope-like compositions comprising, and preferably consisting essentially of, from greater than zero to about 50 weight percent transHFO-1234ze and from about 50 wt.% to less than 100 wt.% propane, more preferably from greater than zero to about 40 wt.% transHFO-1234ze and from about 60 wt.% to less than 100 wt.% propane, and even more preferably from about 1% to about 40 weight percent transHFO-1234ze and from about 60 wt.% to about 99 wt.% propane. In certain preferred embodiments, the azeotrope-like compositions comprise, and preferably consist essentially of, from about 5 wt.% to about 45 wt% transHFO-1234ze and from about 65 wt.% to about 95 wt.% propane.

10 Preferably, the HFO-1234/propane compositions of the present invention have a boiling of from about -40°C to about -43°C at about 14.4 psia.

15 Preferably, the HFO-1234/propane compositions of the present invention have a boiling of about -42°C ±2°C at about 14.4 psia. In certain embodiments, the compositions have a boiling point of preferably about -42°C ±1°C, measured at about 14.4 psia.

20 Preferably the HFO-1234 of these embodiments is transHFO- 1234ze.

HFO-1234/2-Methyl butane

25 In certain other preferred embodiments, the present invention provides compositions, and preferably azeotrope-like compositions comprising transHFO-1234ze and 2-methyl butane. Preferably, such novel azeotrope-like compositions of the present invention comprise, or consist essentially of, effective amounts of transHFO-1234ze and 2-methyl butane. These embodiments preferably provide azeotrope-like compositions comprising, and preferably consisting essentially of from about 90 weight percent to about 99.9 weight percent transHFO-1234ze and from about 0.1 wt.% to about 10 wt.% 2-methyl butane, more

preferably from about 99 wt.% to about 99.9 wt.% transHFO-1234ze and from about 0.1 wt.% to less than 100 wt.% 2- methyl butane.

5 Preferably, the HFO-1234/2- methyl butane compositions of the present invention have a boiling of about -18°C to about -19°C, at about 14.4 psia.

Preferably the HFO-1234/2- methyl butane compositions of the present invention have a boiling of about -18°C ±1°C at about 14.4 psia.

HFO-1234/n-butane

10 In certain other preferred embodiments, the present invention provides compositions, and preferably azeotrope-like compositions comprising transHFO-1234ze and n-butane. Preferably, such novel azeotrope-like compositions of the present invention comprise, or consist essentially of, effective amounts of transHFO-1234ze and n-butane.

15 These embodiments preferably provide azeotrope-like compositions comprising, and preferably consisting essentially of, from about 20 wt.% to about less than 100 wt.% transHFO-1234ze and from greater than zero to about 80 wt.% n-butane, more preferably from about 50 wt.% to about 99 wt.% transHFO-1234ze and from about 1 wt.% to about 50 wt.% n-butane.

20 Preferably, the HFO-1234/n-butane compositions of the present invention have a boiling of from about -19°C to about -22°C at about 14.4 psia.

Preferably, the HFO-1234/n-butane compositions of the present invention have a boiling of about -21°C ±2°C at about 14 psia.

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HFO-1234/isobutane

30 In certain other preferred embodiments, the present invention provides compositions, and preferably azeotrope-like compositions comprising transHFO-1234ze and isobutane. Preferably, such novel azeotrope-like compositions of the present invention comprise, or consist essentially of, effective amounts of transHFO-1234ze and isobutane.

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These embodiments preferably provide azeotrope-like compositions comprising, and preferably consisting essentially of, from about 20 wt.% to about less than 100 wt.% transHFO-1234ze and from greater than zero to about 80 wt.% isobutane, more preferably from about 50 wt.% to about 99 wt.% transHFO-1234ze and from about 1 wt.% to about 50 wt.% isobutane.

Preferably, the HFO-1234/ isobutane compositions of the present invention have a boiling of from about -18°C to about -24°C at about 14 psia.

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Preferably, the HFO-1234/ isobutane compositions of the present invention have a boiling of about -22°C ±2°C at about 14 psia.

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Composition Additives
The compositions, and preferably azeotrope-like compositions of the present invention may further include any of a variety of optional additives including lubricants, stabilizers, metal passivators, corrosion inhibitors, flammability suppressants, and the like.

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According to certain embodiments, the compositions, and preferably azeotrope-like compositions, of the present invention further comprise a stabilizer. Any of a variety of compounds suitable for stabilizing an azeotrope-like composition of the present invention may be used. Examples of certain preferred stabilizers include stabilizer compositions comprising stabilizing diene-based compounds, and/or phenol compounds, and/or epoxides selected from the group consisting of aromatic epoxides, alkyl epoxides, alkenyl epoxides, and combinations of two or more thereof.

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In certain preferred embodiments, the compositions of the present invention further comprise a lubricant. Any of a variety of conventional and unconventional lubricants may be used in the compositions of the present invention. An important requirement for the lubricant is that, when in use in a refrigerant system, there must be sufficient lubricant returning

to the compressor of the system such that the compressor is lubricated. Thus, suitability of a lubricant for any given system is determined partly by the refrigerant/lubricant characteristics and partly by the characteristics of the system in which it is intended to be used. Examples of suitable 5 lubricants include, which are generally those commonly used in refrigeration machinery using or designed to use hydrofluorocarbon (HFC) refrigerants, chlorofluorocarbon refrigerants and hydrochlorofluorocarbons refrigerants, include mineral oil, silicone oil, polyalkyl benzenes (sometimes referred to as (PABs), polyol esters (sometimes referred to as (POEs), polyalkylene glycols (sometimes referred to as (PAGs), polyalkylene glycol esters (sometimes referred to as PAG esters), polyvinyl ethers (sometimes referred to as PVEs), poly(alpha-olefin) (sometimes referred to as PAOs) and halocarbon oils, particularly 10 poly(chlorotrifluorethylene) and the like. Mineral oil, which comprises poly(15 paraffin oil or naphthenic oil, is commercially available. Commercially available mineral oils include Witco LP 250 (registered trademark) from Witco, Zerol 300 (registered trademark) from Shrieve Chemical, Sunisco 3GS from Witco, and Calumet R015 from Calumet. Commercially available polyalkyl benzene lubricants include Zerol 150 (registered 20 trademark). Commercially available esters include neopentyl glycol dipelargonate which is available as Emery 2917 (registered trademark) and Hatcol 2370 (registered trademark). Commercially available PAGs include Motorcraft PAG Refrigerant Compressor Oil, available from Ford, with similar products being available from Dow. Commercially available 25 PAOs include CP-4600 from CPI Engineering. Commercially available PVEs are available from Idemitsu Kosan. Commercially available PAG esters are available from Chrysler. Other useful esters include phosphate esters, dibasic acid esters, and fluoroesters.

For refrigeration systems using or designed to use HFCs, it is 30 generally preferred to use as lubricants PAGs, PAG esters, PVEs, and POEs, particularly for systems comprising compression refrigeration, air-

conditioning (especially for automotive air conditioning) and heat pumps. For refrigeration systems using or designed to use CFCs or HCFCs, it is generally preferred to use as lubricants mineral oil or PAB. In certain preferred embodiments, the lubricants of this invention are organic compounds which are comprised of carbon, hydrogen and oxygen with a ratio of oxygen to carbon and are included to provide, in combination with the amounts used, effective solubility and/or miscibility with the refrigerant to ensure sufficient return of the lubricant to the compressor. This solubility or miscibility preferably exists at at least one temperature from about -30°C and 70°C.

PAGs and PAG esters are highly preferred in certain embodiments because they are currently in use in particular applications such as original equipment mobile air-conditioning systems. Polyol esters are highly preferred in other certain embodiments because they are currently in use in particular non-mobile applications such as residential, commercial, and industrial air conditioning and refrigeration. Of course, different mixtures of different types of lubricants may be used.

Uses of the Compositions

Heat Transfer Compositions and Methods
The present compositions have utility in a wide range of applications. For example, one embodiment of the present invention relates to heat transfer compositions, such as refrigerant compositions, comprising an azeotrope-like composition of the present invention. The heat transfer compositions of the present invention are generally adaptable for use in heat transfer applications, that is, as a heating and/or cooling medium. Although it is contemplated that the compositions of the present invention may include the present azeotrope-like composition in combination with one or more other compounds or combinations of compounds in widely ranging amounts, it is generally preferred that heat transfer compositions of the present invention, including refrigerant

compositions, consist essentially of, and in some embodiments consist of the present azeotrope-like compositions.

The heat transfer compositions of the present invention may be used in any of a wide variety of refrigeration systems including air-conditioning (including both stationary and mobile air conditioning systems), refrigeration, heat-pump systems, and the like. In certain preferred embodiments, the compositions of the present invention are used in refrigeration systems originally designed for use with an HFC-refrigerant or an HCFC refrigerant, such as, for example, HCFC-22. The preferred compositions of the present invention tend to exhibit many of the desirable characteristics of HFC-refrigerants, including non-flammability, and a GWP that is as low, or lower than that of conventional HFC-refrigerants and a capacity that is as substantially similar to or substantially matches, and preferably is as high as or higher than such refrigerants. In particular, applicants have recognized that the present compositions tend to exhibit relatively low global warming potentials (“GWPs”), preferably less than about 1000, more preferably less than about 500, and even more preferably less than about 150. In addition, the relatively constant boiling nature of the compositions of the present invention makes them even more desirable than certain conventional HFCs, such as R-404A or combinations of HFC-32 and R-404A, for use as refrigerants in many applications. Heat transfer compositions of the present invention are particularly preferred as replacements for HFC-134, HFC-22, R-12 and R-500. The present compositions are also believed to be suitable as replacements for the above noted compositions in other applications, such as aerosols, blowing agents and the like.

In certain other preferred embodiments, the present compositions are used in heat transfer systems in general, and in refrigeration systems in particular, originally designed for use with a CFC-refrigerant. Preferred refrigeration compositions of the present invention may be used in refrigeration systems containing a lubricant used conventionally with CFC-

refrigerants, such as mineral oils, polyalkylbenzene, polyalkylene glycols, and the like, or may be used with other lubricants traditionally used with HFC refrigerants.

As used herein the term "refrigeration system" refers generally to any system or apparatus, or any part or portion of such a system or apparatus, which employs a refrigerant to provide cooling. Such refrigeration systems include, for example, air conditioners, electric refrigerators, chillers (including chillers using centrifugal compressors), transport refrigeration systems, commercial refrigeration systems and the like.

In certain embodiments, the compositions of the present invention may be used to retrofit refrigeration systems containing HFC, HCFC, and/or CFC-refrigerants and lubricants used conventionally therewith. Preferably, the present methods involve recharging a refrigerant system that contains a refrigerant to be replaced and a lubricant comprising the steps of (a) removing the refrigerant to be replaced from the refrigeration system while retaining a substantial portion of the lubricant in said system; and (b) introducing to the system a composition of the present invention. As used herein, the term "substantial portion" refers generally to a quantity of lubricant which is at least about 50% (by weight) of the quantity of lubricant contained in the refrigeration system prior to removal of the chlorine-containing refrigerant. Preferably, the substantial portion of lubricant in the system according to the present invention is a quantity of at least about 60% of the lubricant contained originally in the refrigeration system, and more preferably a quantity of at least about 70%. As used herein the term "refrigeration system" refers generally to any system or apparatus, or any part or portion of such a system or apparatus, which employs a refrigerant to provide cooling. Such refrigeration systems include, for example, air conditioners, electric refrigerators, chillers, transport refrigeration systems, commercial refrigeration systems and the like.

Many existing refrigeration systems are currently adapted for use in connection with existing refrigerants, and the compositions of the present invention are believed to be adaptable for use in many of such systems, either with or without system modification. In many applications the 5 compositions of the present invention may provide an advantage as a replacement in smaller systems currently based on certain refrigerants, for example those requiring a small refrigerating capacity and thereby dictating a need for relatively small compressor displacement. Furthermore, in embodiments where it is desired to use a lower capacity 10 refrigerant composition of the present invention, for reasons of efficiency for example, to replace a refrigerant of higher capacity, such embodiments of the present compositions provide a potential advantage. Thus, it is preferred in certain embodiments to use compositions of the present invention, particularly compositions comprising a substantial proportion of, 15 and in some embodiments consisting essentially of the present azeotrope-like compositions, as a replacement for existing refrigerants, such as: CFC-12; HCFC-22; R-404A; R-407C; R-410A; R-500; and R-507A). In certain embodiments it may also be beneficial to use the present compositions in connection with the replacement of R-407A or R-407D. 20 The present compositions are also believed to be suitable as replacements for the above noted compositions in other applications, such as aerosols, blowing agents and the like.

In certain applications, the refrigerants of the present invention potentially permit the beneficial use of larger displacement compressors, 25 thereby resulting in better energy efficiency than other refrigerants, such as Isobutane. Therefore the refrigerant compositions of the present invention provide the possibility of achieving a competitive advantage on an energy basis for refrigerant replacement applications.

It is contemplated that the compositions of the present also have 30 advantage (either in original systems or when used as a replacement for existing refrigerants), in chillers typically used in connection with

commercial air conditioning and refrigeration systems. In certain of such embodiments it is preferred to including in the present compositions from about 0.5 to about 30%, and in certain cases more preferably 0.5% to about 15% by weight of a supplemental flammability suppressant. In this 5 regard it is noted that the HFO-1234ze component and the other compound in the azeotrope-like composition of the present compositions may in certain embodiments act as a flammability suppressant with respect to other components in the composition. For example, in cases where other components more flammable than HFO-1234ze are included 10 in the composition, HFO-1234ze may function to suppress the flammability of such other component. Thus, any additional components which have flammability suppressant functionality in the composition will sometimes be referred to herein as a supplemental flammability suppressant.

In certain embodiments, co-refrigerants, including for example 15 HFCs, HCFCs and CFCs may be included in the heat transfer compositions of the present invention, including one or more of the following compounds, including any and all isomers thereof:

Trichlorofluoromethane (CFC-11)
Dichlorodifluoromethane (CFC-12)
20 Difluoromethane (HFC-32)
1,1,1,3,3-hexafluoropropane (HFC-236fa)
1,1,1,3,3-pentafluoropropane (HFC-245fa)
1,1,1,3,3-pentafluorobutane (HFC-365mfc)
water
25 CO2

The relative amount of any of the above noted components, as well as any additional components which may be included in present compositions, may be incorporated in amounts depending on the particular application for the composition, and all such relative amounts 30 are considered to be within the scope hereof, provided preferably that

such components do not negate the azeotrope-like nature of the preferred compositions described herein.

5 The present methods, systems and compositions are thus adaptable for use in connection with automotive air conditioning systems and devices, commercial refrigeration systems and devices, chillers (including systems which utilize centrifugal compressors), residential refrigerator and freezers, general air conditioning systems, heat pumps, and the like.

10 Any of a wide range of known methods can be used to remove refrigerants to be replaced from a refrigeration system while removing less than a major portion of the lubricant contained in the system. For example, because refrigerants are quite volatile relative to traditional hydrocarbon-based lubricants (the boiling points of refrigerants are generally less than 10°C whereas the boiling points of mineral oils are generally more than 200 °C), in embodiments wherein the lubricant is a hydrocarbon-based lubricant, the removal step may readily be performed by pumping chlorine-containing refrigerants in the gaseous state out of a refrigeration system containing liquid state lubricants. Such removal can be achieved in any of a number of ways known in the art, including, the 15 use of a refrigerant recovery system, such as the recovery system manufactured by Robinair of Ohio. Alternatively, a cooled, evacuated refrigerant container can be attached to the low pressure side of a refrigeration system such that the gaseous refrigerant is drawn into the evacuated container and removed. Moreover, a compressor may be 20 attached to a refrigeration system to pump the refrigerant from the system to an evacuated container. In light of the above disclosure, those of ordinary skill in the art will be readily able to remove chlorine-containing 25 lubricants from refrigeration systems and to provide a refrigeration system having therein a hydrocarbon-based lubricant and substantially no chlorine-containing refrigerant according to the present invention.

Any of a wide range of methods for introducing the present refrigerant compositions to a refrigeration system can be used in the present invention. For example, one method comprises attaching a refrigerant container to the low-pressure side of a refrigeration system and turning on the refrigeration system compressor to pull the refrigerant into the system. In such embodiments, the refrigerant container may be placed on a scale such that the amount of refrigerant composition entering the system can be monitored. When a desired amount of refrigerant composition has been introduced into the system, charging is stopped.

Alternatively, a wide range of charging tools, known to those of skill in the art, is commercially available. Accordingly, in light of the above disclosure, those of skill in the art will be readily able to introduce the refrigerant compositions of the present invention into refrigeration systems according to the present invention without undue experimentation.

According to certain other embodiments, the present invention provides refrigeration systems comprising a refrigerant of the present invention and methods of producing heating or cooling by condensing and/or evaporating a composition of the present invention. In certain preferred embodiments, the methods for cooling including cooling of other fluid either directly or indirectly or a body directly or indirectly, comprise condensing a refrigerant composition comprising an azeotrope-like composition of the present invention and thereafter evaporating said refrigerant composition in the vicinity of the fluid or body to be cooled. Certain preferred methods for heating an article comprise condensing a refrigerant composition comprising an azeotrope-like composition of the present invention in the vicinity of the fluid or body to be heated and thereafter evaporating said refrigerant composition. As used herein, the term "body" is intended to refer not only to inanimate objects but also to living tissue, including animal tissue in general and human tissue in particular. For example, certain aspects of the present invention involved application of the present composition to human tissue for one or more

therapeutic purposes, such as a pain killing technique, as a preparatory anesthetic, or as part of a therapy involving reducing the temperature of the body being treated. In certain embodiments, the application to the body comprises providing the present compositions in liquid form under pressure, preferably in a pressurized container having a one-way discharge valve and/or nozzle, and releasing the liquid from the pressurized container by spraying or otherwise applying the composition to the body. In light of the disclosure herein, those of skill in the art will be readily able to heat and cool articles according to the present inventions without undue experimentation.

Applicants have found that in the systems of the present invention many of the important refrigeration system performance parameters are relatively close to the parameters for many existing refrigeration systems. Those skilled in the art will appreciate the substantial advantage of a low GWP and/or a low ozone depleting refrigerant that can be used as replacement for R-134a or like refrigerants with relatively minimal modifications to the system. It is contemplated that in certain embodiments the present invention provides retrofitting methods which comprise replacing the refrigerant in an existing system with a composition of the present invention, without substantial modification of the system. In certain preferred embodiments the replacement step is a drop-in replacement in the sense that no substantial redesign of the system is required and no major item of equipment needs to be replaced in order to accommodate the refrigerant of the present invention. In certain preferred embodiments, the methods comprise a drop-in replacement in which the capacity of the system is at least about 70%, preferably at least about 85%, and even more preferably at least about 90% of the system capacity prior to replacement. In certain preferred embodiments, the methods comprise a drop-in replacement in which the suction pressure and/or the discharge pressure of the system, and even more preferably both, is/are at least about 70%, more preferably at least about 90% and even more

preferably at least about 95% of the system capacity prior to replacement. In certain preferred embodiments, the methods comprise a drop-in replacement in which the mass flow of the system is at least about 80%, and even more preferably at least 90% of the system capacity prior to replacement.

5

Propellant Compositions and Methods

In another embodiment, the compositions, and preferably azeotrope-like compositions, of this invention may be used as propellants in sprayable compositions, either alone or in combination with known propellants. The propellant composition comprises, more preferably consists essentially of, and, even more preferably, consists of the compositions, and preferably azeotrope-like compositions, of the invention. The active ingredient to be sprayed together with inert ingredients, solvents, lubricants, and other materials may also be present in the sprayable mixture. Preferably, the sprayable composition is an aerosol. Suitable active materials to be sprayed include, without limitation, cosmetic materials such as deodorants, perfumes, hair sprays, and cleaning solvents, as well as medicinal materials such as anti-asthma medications. The term medicinal materials is used herein in its broadest sense to include any and all materials which are, or at least are believed to be, effective in connection with therapeutic, diagnostic, pain relief, and similar treatments, and as such would include for example drugs and biologically active substances.

25

Other Compositions and Methods

Yet another embodiment of the present invention relates to a blowing agent comprising one or more compositions, and preferably azeotrope-like compositions of the invention. In general, the blowing agent may include the azeotrope-like compositions of the present invention in widely ranging amounts. It is generally preferred, however,

that the blowing agents comprise the present azeotrope-like compositions in amounts at least about 5 % by weight, and even more preferably at least about 15 % by weight, of the blowing agent. In certain preferred embodiments, the blowing agent comprises at least about 50% by weight of the present compositions, and in certain embodiments the blowing agent consists essentially of the present azeotrope-like composition. In certain preferred embodiments, the blowing agent includes, in addition to the present compositions, one or more of co-blowing agents, fillers, vapor pressure modifiers, flame suppressants, stabilizers and like adjuvants.

10 In other embodiments, the invention provides foamable compositions. The foamable compositions of the present invention generally include one or more components capable of forming foam having a generally cellular structure and a blowing agent in accordance with the present invention. In certain embodiments, the one or more components comprise a thermosetting composition capable of forming foam and/or foamable compositions. Examples of thermosetting compositions include polyurethane and polyisocyanurate foam compositions, and also phenolic foam compositions. In such thermosetting foam embodiments, one or more of the present azeotrope-like compositions are included as a blowing agent in a foamable composition, or as a part of a two or more part foamable composition, which composition preferably includes one or more additional components capable of reacting and foaming under the proper conditions to form a foam or cellular structure, as is well known in the art. In certain other embodiments, the one or more components comprise thermoplastic materials, particularly thermoplastic polymers and/or resins. Examples of thermoplastic foam components include polyolefins, such as polystyrene (PS), polyethylene (PE), polypropylene (PP) and polyethyleneterephthalate (PET), and foams formed therefrom, preferably low-density foams. In certain embodiments, the thermoplastic foamable composition is an extrudable composition.

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 present 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. Thus, in certain embodiments 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, in certain embodiments, 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.

The invention also relates to foam, and preferably closed cell foam, prepared from a polymer foam formulation containing a composition of the invention, preferably as part of blowing agent.

The present methods and systems also include forming a one component foam, preferably polyurethane foam, containing a blowing agent in accordance with the present invention. In certain preferably embodiments, a portion of the blowing agent is contained in the foam forming agent, preferably by being dissolved in a foam forming agent which is liquid at the pressure within the container, a second portion of the blowing agent is 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. In certain 5 embodiments, such systems and methods 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.

In certain preferred embodiments, dispersing agents, cell stabilizers, 10 surfactants and other additives may also be incorporated into the blowing agent compositions of the present invention. 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 15 those disclosed in U.S. Patent Nos. 2,834,748, 2,917,480, and 2,846,458 .

Other optional additives 20 for the blowing agent mixture may include flame retardants or suppressants 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.

Any of the methods well known in the art, such as those described 25 in "Polyurethanes Chemistry and Technology," Volumes I and II, Saunders and Frisch, 1962, John Wiley and Sons, New York, NY, may be used or adapted for use in accordance with the foam embodiments of the present invention.

Other uses of the present azeotrope-like compositions include use 30 as solvents, cleaning agents, and the like. Those of skill in the art will be readily able to adapt the present compositions for use in such applications without undue experimentation.

EXAMPLES

The invention is further illustrated in the following example which is intended to be illustrative, but not limiting in any manner. For examples 1- 4, a ebulliometer of the general type described by Swietolowski in his book "Ebulliometric Measurements".
5 (Reinhold, 1945) was used.

Example 1

An ebulliometer consisting of vacuum jacketed tube with a
10 condenser on top which is further equipped with a Quartz Thermometer is used. About 9 grams of propane (normal boiling point -42.1C) is charged to the ebulliometer and the boiling temperature is measured. Incremental amounts of HFO-1234ze (99% trans, normal boiling point -19 C) is added in small, measured increments, and after each addition boiling
15 temperature is measured again. Results are reported in Table 1. Each addition of the higher boiling HFO-1234ze should have resulted, in the absence of azeotropic properties, in an increase in the boiling temperature of the mixture. However, temperature depression is observed when HFO-1234 is added to propane, indicating a binary minimum boiling azeotrope
20 is formed, in amounts of from greater than about 0 to about 25 weight percent HFO-1234ze. The boiling point of the composition changed by about 1.1°C or less over the range of from greater than about 0 to about 75 weight percent HFO-1234ze, exhibiting azeotrope and/or azeotrope-like properties over this range at the indicated pressure.

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Table 1
HFO-1234/Propane at 14.47 psia

T (C)	Wt. % Trans-1234ze	Wt. % Propane
-41.58	0	100.00
-42.11	4.38	95.62
-42.62	14.71	85.29
-42.68	24.30	75.70
-42.23	32.40	67.60
-41.71	44.11	55.89
-41.57	52.34	47.66
-41.32	62.37	37.63
-41.12	66.99	33.01
-40.88	71.45	28.55
-40.54	73.29	26.71

5

Example 2

The procedure of Example 1 is repeated, except that about 27 grams of HFO-1234ze (99% trans, normal boiling point -19 C) is charged to the ebulliometer and n-butane (normal boiling point -12 C) is added in small, measured increments, and after each addition boiling temperature is measured again. Results are reported in Table 2. Each addition of the higher boiling n-butane should have resulted, in the absence of azeotropic properties, in an increase in the boiling temperature of the mixture. However, temperature depression is observed when butane is added to the HFO-1234, indicating a binary minimum boiling azeotrope is formed, in amounts of from greater than about 0 to about 10 weight percent n-butane. In addition, the data indicates that a second minimum boiling azeotrope is formed in amounts of from greater than about 35 to about 50 weight percent n-butane. The boiling point of the composition changed by about 2.5°C or less over the range of from greater than about 0 to about 50 weight percent n-butane, exhibiting azeotrope and/or azeotrope-like properties over this range at the indicated pressure.

Table 2
HFO-1234/n-butane at 14.37 psia

T (C)	Wt.% Trans-1234ze	Wt.% n-Butane
-18.63	100	0
-19.32	98.85	1.15
-20.42	97.72	2.28
-21.05	95.79	4.21
-21.30	91.63	8.37
-21.27	88.17	11.83
-21.24	84.21	15.79
-21.17	80.93	19.07
-21.02	75.64	24.36
-20.87	71.26	28.74
-19.33	66.43	33.57

5

Example 3

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The procedure of Example 1 is repeated, except that about 27 grams of isobutane (normal boiling point 12 C) is charged to the ebulliometer and HFO-1234ze (99% trans, normal boiling point -19 C) is added in in small, measured increments, and after each addition boiling temperature is measured again. Results are reported in Table 3. Each addition of the higher boiling isobutane should have resulted, in the absence of azeotropic properties, in an increase in the boiling temperature of the mixture. However, temperature depression is observed when butane is added to the HFO-1234, indicating a binary minimum boiling azeotrope is formed, in amounts of from greater than about 0 to about 50 weight percent isobutane. The boiling point of the composition changed by about 6°C or less over the range of from greater than about 0 to about 50 weight percent isobutane, exhibiting azeotrope and/or azeotrope-like properties over this range at the indicated pressure.

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Table 3
HFO-1234/isobutane at 14.37 psia

T (C)	Wt.% Trans-1234ze	Wt.% Isobutane
-18.02	100.00	0.00
-20.63	98.56	1.44
-22.54	93.81	6.19
-23.54	91.09	8.91
-23.88	83.85	16.15
-23.94	80.95	19.05
-23.97	78.70	21.30
-23.99	73.45	26.55
-23.96	72.09	27.91
-23.92	67.78	32.22
-23.89	65.59	34.41
-23.85	62.14	37.86
-23.74	58.37	41.63
-23.69	54.64	45.36
-23.66	52.85	47.15

5

Example 4

The procedure of Example 1 is repeated, except that about 29 grams of HFO-1234ze (99% trans, normal boiling point -19 C) is charged to the ebulliometer and 2-methylbutane (normal boiling point 28 C) is added in small, measured increments, and after each addition boiling temperature is measured again. Results are reported in Table 4. Each addition of the higher boiling 2-methylbutane should have resulted, in the absence of azeotropic properties, in an increase in the boiling temperature of the mixture. However, temperature depression is observed when 2-methylbutane is added to the HFO-1234, indicating a binary minimum boiling azeotrope is formed, in amounts of from greater than about 0 to about 0.5 weight percent 2-methylbutane. The boiling point of the composition changed by about 0.5C or less over the range of from greater than about 0 to about 1.5 weight percent 2-methylbutane, exhibiting

azeotrope and/or azeotrope-like properties over this range at the indicated pressure.

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Table 4
HFO-1234/2-methylbutane at 14.37 psia

T (C)	Wt.% Trans-1234ze	Wt.% methylbutane
-18.75	100.00	0.00
-18.82	99.89	0.11
-18.80	99.68	0.32
-18.70	99.46	0.54
-18.64	99.03	0.97
-18.62	98.61	1.39

CLAIMS:

1. A foamable composition for forming an extruded thermoplastic foam comprising one or more components capable of forming an extruded thermoplastic foam and blowing agent comprising an azeotrope-like composition comprising (i) trans-1,3,3,3-tetrafluoropropene (transHFO-1234ze) and (ii) a compound selected from the group consisting of propane, n-butane, and isobutane, wherein the boiling point of said azeotrope-like composition is less than the boiling point of either component in the composition.
10
2. The foamable composition as claimed in claim 1 wherein the azeotrope-like composition consists essentially of from greater than zero to 99 weight percent transHFO-1234ze and from 1 weight percent to less than 100 weight percent of a compound selected from the group consisting of propane, n-butane, and isobutane.
15
3. The foamable composition as claimed in claim 2 wherein said azeotrope-like composition comprises from 5 weight percent to 99 weight percent transHFO-1234ze.
4. The foamable composition as claimed in claim 3 wherein said azeotrope-like composition comprises from 20 weight percent to 99 weight percent transHFO-1234ze.
20
5. The foamable composition as claimed in claim 1 wherein said azeotrope-like composition comprises from 20 weight percent to 99 weight percent transHFO-1234ze.
25
6. The foamable composition as claimed in claim 5 wherein said azeotrope-like composition comprises from 1 weight percent to 80 weight percent of a compound selected from the group consisting of n-butane, isobutane and combinations of these.
30
7. The foamable composition as claimed in claim 5 wherein said azeotrope-like composition comprises from 1 weight percent to 80 weight percent of a compound selected from the group consisting of n-butane and isobutane.
- 35 8. The foamable composition of claim 1 wherein said azeotrope-like composition

has a boiling point of from -15°C to -50°C at a pressure of 14.4 psia.

9. The foamable composition of claim 1 wherein said azeotrope-like composition has a boiling point of from -18°C to -45°C at a pressure of 14.4 psia.

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10. The foamable composition as claimed in claim 1 wherein the azeotrope-like composition comprises trans HFO-1234ze and propane, wherein the trans HFO-1234ze is present in an amount of from greater than zero to 75 weight percent.

10

11. The foamable composition according to claim 1 wherein the azeotrope-like composition consists essentially of greater than zero to 50 weight percent transHFO-1234ze and from 50 weight percent to less than 100 weight percent propane.

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12. The foamable composition as claimed in claim 11 wherein said azeotrope-like composition consists essentially of from greater than zero to 40 weight percent trans HFO-1234ze and from 60 weight percent to less than 100 weight percent propane.

20

13. The foamable composition according to claim 1, wherein the azeotropic-like composition comprises trans HFO-1234ze and propane, wherein the trans HFO-1234ze is present in an amount of from greater than zero to 25 weight percent.

25

14. The foamable composition as claimed in claim 11 wherein said azeotrope-like composition comprises from 5 weight percent to 45 weight percent transHFO-1234ze and from 55 weight percent to 95 weight percent propane.

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15. The foamable composition according to claim 11 wherein said azeotrope-like composition has a boiling point of from -40°C to -43°C at a pressure of 14.4 psia.

16. The foamable composition according to claim 11 wherein said azeotrope-like composition has a boiling point of -42°C±2°C at 14.4 psia.

composition consists essentially of from 20 to less than 100 weight percent trans HFO-1234ze and from greater than zero to 80 weight percent n-butane.

19. The foamable composition according to claim 18 wherein said azeotrope-like composition comprises from 50 weight percent to less than 100 weight percent transHFO-1234ze and from greater than zero to 50 weight percent n-butane.
5
20. The foamable composition according to claim 18 wherein said azeotrope-like composition comprises n-butane is present in an amount of from greater than zero to 10 weight percent or from 23 to 50 weight percent.
10
21. The foamable composition according to claim 18 wherein said azeotrope-like composition has a boiling point of from -19°C to -22°C at a pressure of 14.4 psia.
15
22. The foamable composition according to claim 18 wherein said azeotrope-like composition has a boiling point of -21°C±2°C at 14.4 psia.
20
23. The foamable composition according to claim 1 wherein said azeotrope-like composition comprises trans HFO-1234ze and isobutane and wherein the isobutane is present in an amount of from greater than zero to 50 weight percent.
25
24. The foamable composition according to claim 23 wherein said azeotrope-like composition has a boiling point of from -18°C to -24°C at a pressure of 99.3 kPa (14.4 psia).
30
25. The foamable composition according to claim 11 wherein said azeotrope-like composition further comprises at least one adjuvant selected from the group consisting of surfactants, dispersing agents, cell stabilizers, flame retardants, and combinations of two or more of these.
35
26. The foamable composition as claimed in claim 1 wherein the blowing agent comprises at least 5% by weight of the azeotrope-like composition of claim 1 or wherein the blowing agent comprises at least 15% by weight of the azeotrope-like composition of claim 1 or wherein the blowing agent comprises at least 50% by weight of the azeotrope-like composition of claim 1.

27. The foamable composition according to any one of claims 1 to 26 wherein the thermoplastic foam comprises polystyrene, polyethylene, polypropylene or polyethylene terephthalate or combinations thereof.

5

28. The foamable composition according to any one of claims 1 to 26 wherein the thermoplastic foam comprises polystyrene.

10 29. The foamable composition according to any one of claims 1 to 26 wherein the composition has a Global Warming Potential (GWP) of not greater than 150.

30. The foamable composition of claim 1 further comprising at least one additive selected from the group consisting of dispersing agents, cell stabilizers, surfactants, flame retardants and combinations of two or more of these.

15

31. A thermoplastic foam formed from the foamable composition of claim 1.

32. A closed cell thermoplastic foam comprising the foam of claim 31.

20 33. A foam according to claim 31 which is an extruded thermoplastic foam.

34. The foam according to claim 33, wherein the thermoplastic foam comprises polyethylene, polypropylene, polyethylene terephthalate or polystyrene.

25 35. The foam according to claim 33 wherein the thermoplastic foam comprises polystyrene.

36. The thermoplastic foam according to claim 31 wherein the foam is a low density foam.

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37. The thermoplastic foam according to claim 31 wherein the foam is a rigid foam.

38. A closed cell thermoplastic foam comprising the foam of any one of claims 33 to 37.