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DESCRIPTION

FIELD OF THE INVENTION

[0001] This invention relates to compositions falling within claim.

BACKGROUND OF THE INVENTION

[0002] Fluorocarbon based fluids have found widespread use in many commercial and industrial applications. For example, fluorocarbon based fluids are frequently used as a working fluid in systems such as air conditioning, heat pump and refrigeration applications. The vapor compression cycle is one of the most commonly used type methods to accomplish cooling or heating in a refrigeration system. The vapor compression cycle usually involves the phase change of the refrigerant from the liquid to the vapor phase through heat absorption at a relatively low pressure and then from the vapor to the liquid phase through heat removal at a relatively low pressure and temperature, compressing the vapor to a relatively elevated pressure, condensing the vapor to the liquid phase through heat removal at this relatively elevated pressure and temperature, and then reducing the pressure to start the cycle over again.

[0003] While the primary purpose of refrigeration is to remove heat from an object or other fluid at a relatively low temperature, the primary purpose of a heat pump is to add heat at a higher temperature relative to the environment.

[0004] Certain fluorocarbons have been a preferred component in many heat exchange fluids, such as refrigerants, for many years in many applications. For, example, fluoroalkanes, such as chlorofluoromethane and chlorofluoroethane derivatives, have gained widespread use as refrigerants in applications including air conditioning and heat pump applications owing to their unique combination of chemical and physical properties. Many of the refrigerants commonly utilized in vapor compression systems are either single components fluids or azeotropic mixtures.

[0005] Concern has increased in recent years about potential damage to the earth's atmosphere and climate, and certain chlorine-based compounds have been identified as particularly problematic in this regard. The use of chlorine-containing compositions (such as chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs) and the like) as refrigerants in air-conditioning and refrigeration systems has become disfavored because of the ozone-depleting properties associated with many of such compounds. There has thus been an increasing need for new fluorocarbon and hydrofluorocarbon compounds and compositions that offer alternatives for refrigeration and heat pump applications. For example, it has become desirable to retrofit chlorine-containing refrigeration systems by replacing chlorine-containing refrigerants with non-chlorine-containing refrigerant compounds that will not deplete the ozone layer, such as hydrofluorocarbons (HFCs).

[0006] It is generally considered important, however, that any potential substitute refrigerant must also possess those properties present in many of the most widely used fluids, such as excellent heat transfer properties, chemical stability, low- or no- toxicity, non-flammability and lubricant compatibility, among others.

[0007] Applicants have come to appreciate that lubricant compatibility is of particular importance in many of applications. More particularly, it is highly desirably for refrigeration fluids to be compatible with the lubricant utilized in the compressor unit, used in most refrigeration systems. Unfortunately, many non-chlorine-containing refrigeration fluids, including HFCs, are relatively insoluble and/or immiscible in the types of lubricants used traditionally with CFCs and HFCs, including, for example, mineral oils, alkylbenzenes or poly(alpha-olefins). In order for a refrigeration fluid-lubricant combination to work at a desirable level of efficiently within a compression refrigeration, air-conditioning and/or heat pump system, the lubricant should be sufficiently soluble in the refrigeration liquid over a wide range of operating temperatures. Such solubility lowers the viscosity of the lubricant and allows it to flow more easily throughout the system. In the absence of such solubility, lubricants tend to become lodged in the coils of the evaporator of the refrigeration, air-conditioning or heat pump system, as well as other parts of the system, and thus reduce the system efficiency.

[0008] With regard to efficiency in use, it is important to note that a loss in refrigerant thermodynamic performance or energy efficiency may have secondary environmental impacts through increased fossil fuel usage arising from an increased demand for electrical energy.

[0009] Furthermore, it is generally considered desirably for CFC refrigerant substitutes to be effective without major engineering changes to conventional vapor compression technology currently used with CFC refrigerants.

[0010] Flammability is another important property for many applications. That is, it is considered either important or essential in many applications, including particularly in heat transfer applications, to use compositions, which are non-flammable. Thus, it is frequently beneficial to use in such compositions compounds, which are nonflammable. As used herein, the term "nonflammable" refers to compounds or compositions, which are determined to be nonflammable as determined in accordance with ASTM standard E-681, dated 2002. Unfortunately, many HFCs, which might otherwise be desirable for used in refrigerant compositions are not nonflammable. For example, the fluoroalkane difluoroethane (HFC-152a) and the fluoroalkene 1,1,1-trifluoropropene (HFO-1243zf) are each flammable and therefore not viable for use in many applications.

[0011] Higher fluoroalkenes, that is fluorine-substituted alkenes having at least five carbon atoms, have been suggested for use as refrigerants. U.S. Patent No. 4,788,352 - Smutny is directed to production of fluorinated C5 to C8 compounds having at least some degree of unsaturation. The Smutny patent identifies such higher olefins as being known to have utility as refrigerants, pesticides, dielectric fluids, heat transfer fluids, solvents, and intermediates in various chemical reactions. (See column 1, lines 11 - 22).

[0012] While the fluorinated olefins described in Smutny may have some level of effectiveness in heat transfer applications, it is believed that such compounds may also have certain disadvantages. For example, some of these compounds may tend to attack substrates, particularly general-purpose plastics such as acrylic resins and ABS resins. Furthermore, the higher olefinic compounds described in Smutny may also be undesirable in certain applications because of the potential level of toxicity of such compounds which may arise as a result of pesticide activity noted in Smutny. Also, such compounds may have a boiling point, which is too high to make them useful as a refrigerant in certain applications.

[0013] Bromofluoromethane and bromochlorofluoromethane derivatives, particularly bromotrifluoromethane (Halon 1301) and bromochlorodifluoromethane (Halon 1211) have gained widespread use as fire extinguishing agents in enclosed areas such as airplane cabins and computer rooms. However, the use of various halons is being phased out due to their high ozone depletion. Moreover, as halons are frequently used in areas where humans are present, suitable replacements must also be safe to humans at concentrations necessary to suppress or extinguish fire.

[0014] JP 4 110388 A describes heat transfer media comprising fluoroolefins.

[0015] US 5 278 195 A is describes blowing agents comprising fluoroolefins.

[0016] Applicants have thus come to appreciate a need for compositions, and particularly heat transfer compositions, fire extinguishing/suppression compositions, blowing agents, solvent compositions, and compatabilizing agents, that are potentially useful in numerous applications, including vapor compression heating and cooling systems and methods, while avoiding one or more of the disadvantages noted above.

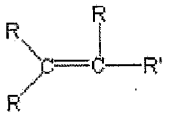
SUMMARY

[0017] Applicants have found that the above-noted need, and other needs, can be satisfied by the claimed compositions.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS THE COMPOSITIONS

[0018] Disclosed herein are the claimed compositions. The claimed compositions can also comprise at least one additional fluoroalkene containing from 3 to 4 carbon atoms, preferably three carbon atoms, and at least one carbon-carbon double bond. The fluoroalkene compounds disclosed herein are sometimes referred to herein for the purpose of convenience as hydrofluoro-olefins or "HFOs" if they contain at least one hydrogen. Although it is contemplated that the HFOs disclosed herein may contain two carbon -- carbon double bonds, such compounds at the present time are not considered to be preferred.

[0019] As mentioned above, the compositions disclosed herein comprise one or more compounds in accordance with Formula I in addition to HFO-1234ze. The compositions disclosed herein may include additional compounds of Formula II below:



(II)

where each R is independently Cl, F, Br, I or H

R' is $(CR_2)nY$,

Y is CRF_2

and n is 0 or 1.

In some compounds disclosed herein, Y is CF_3, n is 0 and at least one of the remaining Rs is F.

[0020] Applicants believe that, in general, the compounds of the above identified Formulas I and II are generally effective and exhibit utility in refrigerant compositions, blowing agent compositions, compatibilizers, aerosols, propellants, fragrances, flavor formulations, and solvent compositions. However, applicants have surprisingly and unexpectedly found that certain of the compounds having a structure in accordance with the formulas described above, e.g. HFO-1234ze, exhibit a highly desirable low level of toxicity compared to other of such compounds. As can be readily appreciated, this discovery is of potentially enormous advantage and benefit for the formulation of not only refrigerant compositions, but also any and all compositions, which would otherwise contain relatively toxic compounds satisfying the formulas described above. More particularly, applicants believe that a relatively low toxicity level is associated with compounds of Formula II, preferably wherein Y is CF_3, wherein at least one R on the unsaturated terminal carbon is H, and at least one of the remaining Rs is F. Applicants believe also that all structural, geometric and stereoisomers of such compounds are effective and of beneficially low toxicity.

[0021] 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.

[0022] Although the properties of cisHFO-1234ze and transHFO-1234ze differ in at least some respects, it is contemplated that each of these compounds is adaptable for use, either alone or together with other compounds including its stereoisomer, in connection with each of the applications, methods and systems described herein. For example, while transHFO-1234ze may be preferred for use in certain refrigeration systems because of its relatively low boiling point (-19° C), it is nevertheless contemplated that cisHFO-1234ze, with a boiling point of +9° C, also has utility in certain refrigeration systems. 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.

[0023] HFO-1234 compounds are known materials and are listed in Chemical Abstracts databases. The production of fluoropropenes such as $CF_3CH=CH_2$ 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 1,1,1,3-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" bearing attorney docket number (H0003789 (26267)).

[0024] The compositions disclosed herein are believed to possess properties that are advantageous for a number of important reasons. For example, applicants believe, based at least in part on mathematical modeling, that HFO-1234ze will not have a substantial negative affect on atmospheric chemistry, being negligible contributors to ozone depletion in comparison to some other halogenated species. The compositions of the present invention thus have the advantage of not contributing substantially to ozone depletion. The preferred compositions also do not contribute substantially to global warming compared to many of the hydrofluoroalkanes presently in use.

[0025] Compositions of the present invention have a Global Warming Potential (GWP) of not greater than 1000, more preferably not greater than 500, and even more preferably not greater than 150. In certain embodiments, the GWP of the present compositions is not greater than 100 and even more preferably not greater than 75. As used herein, "GWP" is measured relative to that of carbon dioxide and over a 100-year time horizon, as defined in "The Scientific Assessment of Ozone Depletion, 2002, a report of the World Meteorological Association's Global Ozone Research and Monitoring Project,".

[0026] In certain preferred forms, the present compositions also preferably have an Ozone Depletion Potential (ODP) of not greater than 0.05, more preferably not greater than 0.02 and even more preferably about zero. As used herein, "ODP" is as defined in "The Scientific Assessment of Ozone Depletion, 2002, A report of the World Meteorological Association's Global Ozone Research and Monitoring Project," .

[0027] The amount of the Formula I compounds, particularly HFO-1234, contained in the compositions disclosed herein, can vary widely, depending the particular application, and compositions containing more than trace amounts and less than 100% of the compound are within broad the scope of the present invention. Moreover, the compositions of the present invention can be azeotropic, azeotrope-like or non-azeotropic. The present compositions comprise HFO-1234ze, in amounts from 5% by weight to 99% by weight, and even more preferably from 5% to 95%.

[0028] Many additional compounds may be included in the present compositions, and the presence of all such compounds is within the broad scope of the invention. The present compositions can include, in addition to HFO-1234ze and 1,1,1,2-Tetrafluoroethane (HFC-134a), one or more of the following:

Difluoromethane (HFC-32)

Pentafluoroethane (HFC-125)

1,1,2,2-tetrafluoroethane (HFC-134)

Difluoroethane (HFC-152a)

1,1,1,2,3,3,3-Heptafluoropropane (HFC-227ea)

1,1,1,3,3,3-hexafluoropropane (HFC-236fa)

1,1,1,3,3-pentafluoropropane (HFC-245fa)

1,1,1,3,3-pentafluorobutane (HFC-365mfc)

water

CO_2

[0029] The relative amount of any of the above noted components, as well as any additional components which may be included in present compositions, can vary widely within the general broad scope of claim 1 according to the particular application for the composition, and all such relative amounts are considered to be within the scope hereof.

HEAT TRANSFER COMPOSITIONS

[0030] Although it is contemplated that the compositions of claim 1 may include the compounds of the present disclosure in widely ranging amounts, it is generally preferred that refrigerant compositions of the present invention comprise HFO-1234ze, in an amount that is at least about 50% by weight, and even more preferably at least about 70 % by weight, of the composition. It is preferred that the heat transfer compositions of the present invention comprise transHFO-1234ze. It is preferred that heat transfer compositions of the present invention comprise a combination of cisHFO-1234ze and transHFO1234ze in a cis:trans weight ratio of from about 1:99 to about 10:99, more preferably from about 1:99 to about 5:95, and even more preferably from about 1:99 to about 3:97.

[0031] The compositions of the present invention may include other components for the purpose of enhancing or providing certain functionality to the composition, or in some cases to reduce the cost of the composition. For example, refrigerant compositions according to the present invention, especially those used in vapor compression systems, include a lubricant, generally in amounts of from about 30 to about 50 percent by weight of the composition. Furthermore, the present compositions may also include a compatibilizer, such as propane, for the purpose of aiding compatibility and/or solubility of the lubricant. Such compatibilizers, including propane, butanes and pentanes, are preferably present in amounts of from about 0.5 to about 5 percent by weight of the composition. Combinations of surfactants and solubilizing agents may also be added to the present compositions to aid oil solubility, as disclosed by U.S. Patent No. 6,516,837. Commonly used refrigeration lubricants such as Polyol Esters (POEs) and Poly Alkylene Glycols (PAGs), silicone oil, mineral oil, alkyl benzenes (ABs) and poly(alpha-olefin) (PAO) that are used in refrigeration machinery with hydrofluorocarbon (HFC) refrigerants may be used with the refrigerant compositions of the present invention.

[0032] 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 compositions of the present invention may provide an advantage as a replacement in systems, which are currently based on refrigerants having a relatively high capacity. Furthermore, in embodiments where it is desired to use a lower capacity refrigerant composition of the present invention, for reasons of cost for example, to replace a refrigerant of higher capacity, such embodiments of the present the compositions provide a potential advantage. Thus, compositions of the present invention, particularly compositions comprising a substantial proportion of, of transHFO-1234ze, are used as a replacement for existing refrigerants, such as HFC-134a. In certain applications, the refrigerants of the present invention potentially permit the beneficial use of larger displacement compressors, thereby resulting in better energy efficiency than other refrigerants, such as HFC-134a. Therefore the refrigerant compositions of the present invention, particularly compositions comprising transHFO-1234ze, provide the possibility of achieving a competitive advantage on an energy basis for refrigerant replacement applications.

[0033] It is contemplated that the compositions comprising HFO-1234ze, also have advantage (either in original systems or when used as a replacement for refrigerants such as R-12 and R-500), in chillers typically used in connection with commercial air conditioning systems. In certain of such embodiments it is preferred to including in the present HFO-1234ze compositions from 0.5 to 5% of a flammability suppressant, such as CF3I.

[0034] The methods, systems disclosed herein and the present compositions are thus adaptable for use in connection with automotive air conditioning systems and devices, commercial refrigeration systems and devices, chillers, residential refrigerator and freezers, general air conditioning systems, heat pumps, and the like.

BLOWING AGENTS, FOAMS AND FOAMABLE COMPOSITIONS

[0035] Blowing agents may also comprise or constitute one or more of the claimed compositions. As mentioned above, the claimed compositions may include the compounds of the present disclosure in widely ranging amounts. Compositions for use as blowing agents in accordance with the present invention contain HFO-1234ze in an amount that is at least 5 % by weight to 95 % by weight, and even more preferably at least about 15 % by weight, of the composition. In certain preferred embodiments, the blowing agent compositions include, in addition to HFO-1234ze and HFC-134a one or more of the following components as a co-blowing agent, filler, vapor pressure modifier, or for any other purpose:

Difluoromethane (HFC-32)

Pentafluoroethane (HFC-125)

1,1,2,2-tetrafluoroethane (HFC-134)

Difluoroethane (HFC-152a)

1,1,1,2,3,3,3-Heptafluoropropane (HFC-227ea)

1,1,1,3,3,3-hexafluoropropane (HFC-236fa)

1,1,1,3,3-pentafluoropropane (HFC-245fa)

1,1,1,3,3-pentafluorobutane (HFC-365mfc)

water

CO_2

[0036] It is contemplated that the blowing agent compositions of the present disclosure may comprise cisHFO-1234ze, transHFO1234ze or combinations thereof. In certain preferred embodiments, the blowing agent composition of the present invention comprise his a combination of cisHFO-1234ze and transhFO1234ze in a cis:trans weight ratio of from about 1:99 to about 10:99, and even more preferably from about 1:99 to about 5:95.

[0037] In other embodiments, the disclosure provides foamable compositions, and preferably polyurethane, polyisocyanurate and extruded thermoplastic foam compositions, prepared using the compositions of the present invention. In such foam embodiments, one or more of the claimed compositions are included as or part of a blowing agent in a foamable composition, which composition preferably includes one or more additional components capable of reacting and/or foaming under the proper conditions to form a foam or cellular structure, as is well known in the art. The disclosure also relates to foam, and preferably closed cell foam, prepared from a polymer foam formulation containing a blowing agent comprising the compositions of the invention. In yet other embodiments, the invention provides foamable compositions comprising thermoplastic or polyolefin foams, such as polystyrene (PS), polyethylene (PE), polypropylene (PP) and polyethyleneterpthalate (PET) foams, preferably low-density foams.

[0038] In certain preferred embodiments, dispersing agents, cell stabilizers, 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 copolymers such as those disclosed in U.S. Patent Nos. 2,834,748, 2,917,480. 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.

PROPELLANT AND AEROSOL COMPOSITIONS

[0039] In another aspect, the present disclosure provides propellant compositions comprising or consisting essentially of a claimed composition, such propellant composition preferably being a sprayable composition. The propellant compositions preferably comprise a material to be sprayed and a propellant comprising, consisting essentially of, or consisting of a claimed composition. Inert ingredients, solvents, and other materials may also be present in the sprayable mixture. Preferably, the sprayable composition is an aerosol. Suitable materials to be sprayed include, without limitation, cosmetic materials such as deodorants, perfumes, hair sprays, cleansers, and polishing agents as well as medicinal materials such as anti-asthma components, anti-halitosis components and any other medication or the like, including preferably any other medicament or agent intended to be inhaled. The medicament or other therapeutic agent is preferably present in the composition in a therapeutic amount, with a substantial portion of the balance of the composition comprising HFO-1234ze.

[0040] Aerosol products for industrial, consumer or medical use typically contain one or more propellants along with one or more active ingredients, inert ingredients or solvents. The propellant provides the force that expels the product in aerosolized form. While some aerosol products are propelled with compressed gases like carbon dioxide, nitrogen, nitrous oxide and even air, most commercial aerosols use liquefied gas propellants. The most commonly used liquefied gas propellants are hydrocarbons such as butane, isobutane, and propane. Dimethyl ether and HFC-152a (1, 1-difluoroethane) are also used, either alone or in blends with the hydrocarbon propellants. Unfortunately, all of these liquefied gas propellants are highly flammable and their incorporation into aerosol formulations will often result in flammable aerosol products.

[0041] Applicants have come to appreciate the continuing need for nonflammable, liquefied gas propellants with which to formulate aerosol products. The present disclosure provides compositions comprising HFO-1234ze, for use in certain industrial aerosol products, including for example spray cleaners, lubricants, and the like, and in medicinal aerosols, including for example to deliver medications to the lungs or mucosal membranes. Examples of this includes metered dose inhalers (MDIs) for the treatment of asthma and other chronic obstructive pulmonary diseases and for delivery of medicaments to accessible mucous membranes or intranasally. Also disclosed herein are methods for treating ailments, diseases and similar health related problems of an organism (such as a human or animal) comprising applying a composition of the present invention containing a medicament or other therapeutic component to the organism in need of treatment. In certain methods disclosed herein, the step of applying the present composition comprises providing a MDI containing the composition of the present invention (for example, introducing the composition into the MDI) and then discharging the present composition from the MDI.

[0042] The claimed compositions are capable of providing nonflammable, liquefied gas propellant and aerosols that do not contribute substantially to global warming. The claimed compositions can be used to formulate a variety of industrial aerosols or other sprayable compositions such as contact cleaners, dusters, lubricant sprays, and the like, and consumer aerosols such as personal care products, household products and automotive products. HFO-1234ze is particularly preferred for use as an important component of propellant compositions for in medicinal aerosols such as metered dose inhalers. The medicinal aerosol and/or propellant and/or sprayable compositions many applications include, in addition to HFO-1234ze, a medicament such as a beta-agonist, a corticosteroid or other medicament, and, optionally, other ingredients, such as surfactants, solvents, other propellants, flavorants and other excipients. The claimed compositions, unlike many compositions previously used in these applications, have good environmental properties and are not considered to be potential contributors to global warming. The present compositions therefore provide in certain preferred embodiments substantially nonflammable, liquefied gas propellants having very low Global Warming potentials.

FLAVORANTS AND FRAGRANCES

[0043] The claimed compositions also provide advantage when used as part of, and in particular as a carrier for, flavor formulations and fragrance formulations. The suitability of the present compositions for this purpose is demonstrated by a test procedure in which 0.39 grams of Jasmone were put into a heavy walled glass tube. 1.73 grams of R-1234ze were added to the glass tube. The tube was then frozen and sealed. Upon thawing the tube, it was found that the mixture had one liquid phase. The solution contained 20 wt. % Jasome and 80 wt. % R-1234ze, thus establishing its favorable use as a carrier or part of delivery system for flavor formulations, in aerosol and other formulations. It also establishes its potential as an extractant of fragrances, including from plant matter.

METHODS AND SYSTEMS

[0044] The claimed compositions are useful in connection with numerous methods and systems, including as heat transfer fluids in methods and systems for transferring heat, such as refrigerants used in refrigeration, air conditioning and heat pump systems. The present compositions are also advantageous for in use in systems and methods of generating aerosols, preferably comprising or consisting of the aerosol propellant in such systems and methods. Methods of forming foams and methods of extinguishing and suppressing fire are also disclosed herein. The methods disclosed herein also provide methods of removing residue from articles in which the present compositions are used as solvent compositions in such methods and systems.

HEAT TRANSFER METHODS

[0045] The heat transfer methods disclosed herein generally comprise providing a claimed composition and causing heat to be transferred to or from the composition changing the phase of the composition. For example, the methods disclosed herein provide cooling by absorbing heat from a fluid or article, preferably by evaporating the present refrigerant composition in the vicinity of the body or fluid to be cooled to produce vapor comprising the present composition. The methods disclosed herein may include the further step of compressing the refrigerant vapor, usually with a compressor or similar equipment to produce vapor of the present composition at a relatively elevated pressure. Generally, the step of compressing the vapor results in the addition of heat to the vapor, thus causing an increase in the temperature of the relatively high-pressure vapor. The methods disclosed herein include removing from this relatively high temperature, high pressure vapor at least a portion of the heat added by the evaporation and compression steps. The heat removal step preferably includes condensing the high temperature, high-pressure vapor while the vapor is in a relatively high-pressure condition to produce a relatively high-pressure liquid comprising a composition of the present invention. This relatively high-pressure liquid preferably then undergoes a nominally isoenthalpic reduction in pressure to produce a relatively low temperature, low-pressure liquid. In such methods, it is this reduced temperature refrigerant liquid which is then vaporized by heat transferred from the body or fluid to be cooled.

[0046] In another process disclosed herein, the claimed compositions may be used in a method for producing heating which comprises condensing a refrigerant comprising the compositions in the vicinity of a liquid or body to be heated. Such methods, as mentioned hereinbefore, frequently are reverse cycles to the refrigeration cycle described above.

FOAM BLOWING METHODS

[0047] Disclosed herein are methods of forming foams, and preferably polyurethane and polyisocyanurate foams.

[0048] The methods disclosed herein generally comprise providing a blowing agent composition falling within the claims, 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, may be used or adapted for use in accordance with the foams disclosed herein. In general, the methods disclosed herein may comprise preparing polyurethane or polyisocyanurate foams by combining an isocyanate, a polyol or mixture of polyols, a blowing agent or mixture of blowing agents comprising one or more of the present compositions, and other materials such as catalysts, surfactants, and optionally, flame retardants, colorants, or other additives.

[0049] It is convenient in many applications to provide the components for polyurethane or polyisocyanurate foams in pre-blended formulations.

[0050] Most typically, the foam formulation is pre-blended into two components. The isocyanate and optionally certain surfactants and blowing agents comprise the first component, commonly referred to as the "A" component.

[0051] The polyol or polyol mixture, surfactant, catalysts, blowing agents, flame retardant, and other isocyanate reactive components comprise the second component, commonly referred to as the "B" component. Accordingly, polyurethane or polyisocyanurate foams are readily prepared by bringing together the A and B side components either by hand mix for small preparations and, preferably, machine mix techniques to form blocks, slabs, laminates, pour-in-place panels and other items, spray applied foams, froths, and the like. Optionally, other ingredients such as fire retardants, colorants, auxiliary blowing agents, and even other polyols can be added as a third stream to the mix head or reaction site. Most preferably, however, they are all incorporated into one B-component as described above.

[0052] It is also possible to produce thermoplastic foams using the claimed compositions. For example, conventional polystyrene and polyethylene formulations may be combined with the compositions in a conventional manner to produce rigid foams.

CLEANING METHODS

[0053] Also disclosed herein are methods of removing containments from a product, part, component, substrate, or any other article or portion thereof by applying to the article a composition falling within the claims. For the purposes of convenience, the term "article" is used herein to refer to all such products, parts, components, substrates, and the like and is further intended to refer to any surface or portion thereof. Furthermore, the term "contaminant" is intended to refer to any unwanted material or substance present on the article, even if such substance is placed on the article intentionally. For example, in the manufacture of semiconductor devices it is common to deposit a photoresist material onto a substrate to form a mask for the etching operation and to subsequently remove the photoresist material from the substrate. The term "contaminant" as used herein is intended to cover and encompass such a photo resist material.

[0054] Preferred methods disclosed herein comprise applying the claimed composition to the article. Although it is contemplated that numerous and varied cleaning techniques can employ the compositions of the present invention to good advantage, it is considered to be particularly advantageous to use the claimed compositions in connection with supercritical cleaning techniques. Supercritical cleaning is disclosed in US Patent No. 6,589,355, which is assigned to the assignee of the present invention. For supercritical cleaning applications, is preferred in certain methods disclosed herein to include in the present cleaning compositions one or more additional components, such as CO_2 and other additional components known for use in connection with supercritical cleaning applications. It may also be possible and desirable in certain methods disclosed herein to use the present cleaning compositions in connection with particular vapor degreasing and solvent cleaning methods.

FLAMMABILITY REDUCTION METHODS

[0055] Also disclosed are methods for reducing the flammability of fluids, said methods comprising adding a composition falling within the claims to said fluid. The flammability associated with any of a wide range of otherwise flammable fluids may be reduced according to the methods disclosed herein. For example, the flammability associated with fluids such as ethylene oxide, flammable hydrofluorocarbons and hydrocarbons, including: HFC-152a, 1,1,1-trifluoroethane (HFC-143a), difluoromethane (HFC-32), propane, hexane, octane, and the like can be reduced according to the method disclosed herein. For the purposes of the methods disclosed herein, a flammable fluid may be any fluid exhibiting flammability ranges in air as measured via any standard conventional test method, such as ASTM E-681, and the like.

[0056] Any suitable amounts of the present compositions may be added to reduce flammability of a fluid according to the methods disclosed herein. As will be recognized by those of skill in the art, the amount added will depend, at least in part, on the degree to which the subject fluid is flammable and the degree to which it is desired to reduce the flammability thereof. In certain preferred methods disclosed herein, the amount of composition added to the flammable fluid is effective to render the resulting fluid substantially non-flammable.

FLAME SUPPRESSION METHODS

[0057] Further disclosed herein are methods of suppressing a flame, said methods comprising contacting a flame with a fluid comprising a composition falling within claim 1. Any suitable methods disclosed herein for contacting the flame with the claimed composition may be used. For example, the composition may be sprayed, poured, and the like onto the flame, or at least a portion of the flame may be immersed in the composition. In light of the teachings herein, those of skill in the art will be readily able to adapt a variety of conventional apparatus and methods of flame suppression for use in the methods disclosed herein.

STERILIZATION METHODS

[0058] Many articles, devices and materials, particularly for use in the medical field, must be sterilized prior to use for the health and safety reasons, such as the health and safety of patients and hospital staff. Disclosed herein are methods of sterilizing comprising contacting the articles, devices or material to be sterilized with a composition falling within claim 1, in combination with one or more sterilizing agents. While many sterilizing agents are known in the art and are considered to be adaptable for use in connection with the methods disclosed herein, in certain preferred methods disclosed herein sterilizing agent comprises ethylene oxide, formaldehyde, hydrogen peroxide, chlorine dioxide, ozone and combinations of these. In certain methods disclosed herein, ethylene oxide is the preferred sterilizing agent. Those skilled in the art, in view of the teachings contained herein, will be able to readily determine the relative proportions of sterilizing agent and the present compositions to be used in connection with the present sterilizing compositions and methods disclosed herein, and all such ranges are within the broad scope hereof. As is known to those skilled in the art, certain sterilizing agents, such as ethylene oxide, are relatively flammable components, and the present compositions are included in amounts effective, together with other components present in the composition, to reduce the flammability of the sterilizing composition to acceptable levels.

[0059] The sterilization methods disclosed herein may be either high or low-temperature sterilization methods involving the use of a composition according to claim 1 at a temperature of from about 121°C (250°F)to about 132°C (270°F), preferably in a substantially sealed chamber. The process can be completed usually in less than about 2 hours. However, some articles, such as plastic articles and electrical components, cannot withstand such high temperatures and require low-temperature sterilization. In low temperature sterilization methods disclosed herein, the article to be sterilized is exposed to a fluid comprising a composition of the present invention at a temperature of from about room temperature to about 93°C (200°F), more preferably at a temperature of from about room temperature to about 38°C (100°F).

[0060] The low-temperature sterilization disclosed herein is preferably at least a two-step process performed in a substantially sealed, preferably air tight, chamber. In the first step (the sterilization step), the articles having been cleaned and wrapped in gas permeable bags are placed in the chamber. Air is then evacuated from the chamber by pulling a vacuum and perhaps by displacing the air with steam. In certain methods disclosed herein, it is preferable to inject steam into the chamber to achieve a relative humidity that ranges preferably from about 30% to about 70%. Such humidities may maximize the sterilizing effectiveness of the sterilant, which is introduced into the chamber after the desired relative humidity is achieved. After a period of time sufficient for the sterilant to permeate the wrapping and reach the interstices of the article, the sterilant and steam are evacuated from the chamber.

[0061] In the preferred second step of the process (the aeration step), the articles are aerated to remove sterilant residues. Removing such residues is particularly important in the case of toxic sterilants, although it is optional in those cases in which the substantially non-toxic compositions of the present invention are used. Typical aeration processes include air washes, continuous aeration, and a combination of the two. An air wash is a batch process and usually comprises evacuating the chamber for a relatively short period, for example, 12 minutes, and then introducing air at atmospheric pressure or higher into the chamber. This cycle is repeated any number of times until the desired removal of sterilant is achieved. Continuous aeration typically involves introducing air through an inlet at one side of the chamber and then drawing it out through an outlet on the other side of the chamber by applying a slight vacuum to the outlet. Frequently, the two approaches are combined. For example, a common approach involves performing air washes and then an aeration cycle.

EXAMPLES

REFERENCE EXAMPLE 1

[0062] The coefficient of performance (COP) is a universally accepted measure of refrigerant performance, especially useful in representing the relative thermodynamic efficiency of a refrigerant in a specific heating or cooling cycle involving evaporation or condensation of the refrigerant. In refrigeration engineering, this term expresses the ratio of useful refrigeration to the energy applied by the compressor in compressing the vapor. The capacity of a refrigerant represents the amount of cooling or heating it provides and provides some measure of the capability of a compressor to pump quantities of heat for a given volumetric flow rate of refrigerant. In other words, given a specific compressor, a refrigerant with a higher capacity will deliver more cooling or heating power. One means for estimating COP of a refrigerant at specific operating conditions is from the thermodynamic properties of the refrigerant using standard refrigeration cycle analysis techniques (see for example, R.C. Downing, FLUOROCARBON REFRIGERANTS HANDBOOK, Chapter 3, Prentice-Hall, 1988).

[0063] A refrigeration /air conditioning cycle system is provided where the condenser temperature is about 66°C (150°F) and the evaporator temperature is about -37°C (-35°F) under nominally isentropic compression with a compressor inlet temperature of about 10°C (50°F). COP is determined for several compositions of the present invention over a range of condenser and evaporator temperatures and reported in Table I below, based upon HFC-134a having a COP value of 1.00, a capacity value of 1.00 and a discharge temperature of 79°C (175 °F).

TABLE I

REFRIGERANT COMPOSITION	Relative COP	Relative CAPACITY	DISCHARGE TEMPERATURE (°C)
HFO 1225ye	1.02	0.76	70°C (158°F)
HFO trans-1234ze	1.04	0.70	74°C (165°F)
HFO cis-1234ze	1.13	0.36	68°C (155°F)
HFO 1234yf	0.98	1.10	76°C (168°F)

[0064] This example shows that certain compounds have a better energy efficiency than HFC-134a (1.02, 1.04 and 1.13 compared to 1.00) and the compressor using the present refrigerant compositions will produce discharge temperatures (70°C (158°F), 74°C (165°F) and 68°C (155°F) compared to 79°C (175°F)), which is advantageous since such result will likely leading to reduced maintenance problems.

REFERENCE EXAMPLE 2

[0065] The miscibility of HFO-1225ye and HFO-1234ze with various refrigeration lubricants is tested. The lubricants tested are mineral oil (C3), alkyl benzene (Zerol 150), ester oil (Mobil EAL 22 cc and Solest 120), polyalkylene glycol (PAG) oil (Goodwrench Refrigeration Oil for 134a systems), and a poly(alpha-olefin) oil (CP-6005-100). For each refrigerant/oil combination, three compositions are tested, namely 5, 20 and 50 weight percent of lubricant, with the balance of each being the compound of the present invention being tested.

[0066] The lubricant compositions are placed in heavy-walled glass tubes. The tubes are evacuated, the refrigerant compound in accordance with the present invention is added, and the tubes are then sealed. The tubes are then put into an air bath environmental chamber, the temperature of which is varied from about -50°C to 70°C. At roughly 10°C intervals, visual observations of the tube contents are made for the existence of one or more liquid phases. In a case where more than one liquid phase is observed, the mixture is reported to be immiscible. In a case where there is only one liquid phase observed, the mixture is reported to be miscible.

[0067] In those cases where two liquid phases were observed, but with one of the liquid phases occupying only a very small volume, the mixture is reported to be partially miscible.

[0068] The polyalkylene glycol and ester oil lubricants were judged to be miscible in all tested proportions over the entire temperature range, except that for the HFO-1225ye mixtures with polyalkylene glycol, the refrigerant mixture was found to be immiscible over the temperature range of -50°C to -30°C and to be partially miscible over from -20 to 50°C. At 50 weight percent concentration of the PAG in refrigerant and at 60°, the refrigerant/PAG mixture was miscible. At 70°C, it was miscible from 5 weight percent lubricant in refrigerant to 50 weight percent lubricant in refrigerant.

REFERENCE EXAMPLE 3

[0069] The compatibility of the refrigerant compounds and compositions of the present invention with PAG lubricating oils while in contact with metals used in refrigeration and air conditioning systems is tested at 350° C, representing conditions much more severe than are found in many refrigeration and air conditioning applications.

[0070] Aluminum, copper and steel coupons are added to heavy walled glass tubes. Two grams of oil are added to the tubes. The tubes are then evacuated and one gram of refrigerant is added. The tubes are put into an oven at 188°C (350°F) for one week and visual observations are made. At the end of the exposure period, the tubes are removed.

[0071] This procedure was done for the following combinations of oil and the compound of the present invention:

1. a) HFO-1234ze and GM Goodwrench PAG oil
2. b) HFO1243 zf and GM Goodwrench oil PAG oil
3. c) HFO-1234ze and MOPAR-56 PAG oil
4. d) HFO-1243 zf and MOPAR-56 PAG oil
5. e) HFO-1225 ye and MOPAR-56 PAG oil.

[0072] In all cases, there is minimal change in the appearance of the contents of the tube. This indicates that the refrigerant compounds and compositions of the present invention are stable in contact with aluminum, steel and copper found in refrigeration and air conditioning systems, and the types of lubricating oils that are likely to be included in such compositions or used with such compositions in these types of systems.

COMPARATIVE EXAMPLE

[0073] Aluminum, copper and steel coupons are added to a heavy walled glass tube with mineral oil and CFC-12 and heated for one week at 350°C, as in Example 3. At the end of the exposure period, the tube is removed and visual observations are made. The liquid contents are observed to turn black, indicating there is severe decomposition of the contents of the tube.

[0074] CFC-12 and mineral oil have heretofore been the combination of choice in many refrigerant systems and methods. Thus, the refrigerant compounds and compositions of the present invention possess significantly better stability with many commonly used lubricating oils than the widely used prior art refrigerant-lubricating oil combination.

REFERENCE EXAMPLE 4 - POLYOL FOAM

[0075] This example illustrates the use of blowing agent in accordance with one of the preferred embodiments of the present invention, namely the use of HFO-1234ze, and the production of polyol foams in accordance with the present invention. The components of a polyol foam formulation are prepared in accordance with the following table:

Polvol Component*	**PBW**
Voranol 490	50
Voranol 391	50
Water	0.5
B-8462 (surfactant)	2.0
Polycat 8	0.3
Polycat 41	3.0
HFO-1234ze	35
Total	140.8

Isocyanate

[0076]

M-20S	123.8 Index 1.10

[0077] *Voranol 490 is a sucrose-based polyol and Voranol 391 is a toluene diamine based polyol, and each are from Dow Chemical. B-8462 is a surfactant available from Degussa-Goldschmidt. Polycat catalysts are tertiary amine based and are available from Air Products. Isocyanate M-20S is a product of Bayer LLC.

[0078] The foam is prepared by first mixing the ingredients thereof, but without the addition of blowing agent. Two Fisher-Porter tubes are each filled with about 52.6 grams of the polyol mixture (without blowing agent) and sealed and placed in a refrigerator to cool and form a slight vacuum. Using gas burets, about 17.4 grams of HFO-1234ze are added to each tube, and the tubes are then placed in an ultrasound bath in warm water and allowed to sit for 30 minutes. The solution produced is hazy, a vapor pressure measurement at room temperature indicates a vapor pressure of about 580 kPa (70 psig), indicating that the blowing agent is not in solution. The tubes are then placed in a freezer at 3°C (27° F) for 2 hours.

[0079] The vapor pressure was again measured and found to be 200 kPa (14-psig). The isocyanate mixture, about 87.9 grams, is placed into a metal container and placed in a refrigerator and allowed to cool to about 10°C (50°F). The polyol tubes were then opened and weighed into a metal mixing container (about 100 grams of polyol blend are used). The isocyanate from the cooled metal container is then immediately poured into the polyol and mixed with an air mixer with double propellers at 3000 RPM's for 10 seconds. The blend immediately begins to froth with the agitation and is then poured into a 20x20x10 cm (8x8x4 inch)box and allowed to foam. Because of the froth, a cream time cannot be measured. The foam has a 4-minute gel time and a 5-minute tack free time. The foam is then allowed to cure for two days at room temperature.

[0080] The foam is then cut to samples suitable for measuring physical properties and is found to have a density of 34.3 kg/m^3 (2.14 pcf). K-factors are measured and found to be as follows:

Temperature	K, BTU In / Ft^2 h °F
4.4°C (40°F)	.1464
24°C (75°F)	.1640
43°C (110°F)	.1808

REFERENCE EXAMPLE 5 - POLYSTYRENE FOAM

[0081] This example illustrates the use of blowing agent in accordance with two preferred embodiments of the present invention, namely the use of HFO-1234ze and HFO-1234-yf, and the production of polystyrene foam. 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 consisting essentially of HFO-1234ze 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 flangesand a section of 5 cm (2-inch) diameter schedule 40 stainless steel pipe 10 cm (4 inches) long (see Figure 1). The vessel is placed in an oven, with temperature set at from about 88°C (190°F) to about 141 °C (285°F), preferably for polystyrene at 129°C (265°F), and remains there until temperature equilibrium is reached.

[0082] 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 two foams thus produced using this method are given in Table 1 and graphed in Figure 1 as the density of the foams produced using trans-HFO-1234ze and HFO-1234yf. The data show that foam polystyrene is obtainable in accordance with the present invention. The die temperature for R1234ze with polystyrene is about 121 °C (250°F).

Table 1

	Dow polystyrene 685D	
	Foam density Kg/m^3 (lb/ft^3)	
T°C (°F)	transHFO-1234ze	HFO-1234yf
135 (275)	883.4 (55.15)	
127 (260)	354.7 (22.14)	228.6 (14.27)
121 (250)	116 (7.28)	387.2 (24.17)
116 (240)	217.2 (16.93)	

REFERENCES CITED IN THE DESCRIPTION

Cited references

Patent documents cited in the description

- US4788352A [0011]
- JP4110388A [0014]
- US5278195A [0015]
- US2889379A [0023]
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- US6589355B [0054]

SAMMENSÆTNINGER MED HFO-1234ZE OG HFC-134A

PATENTKRAV

1. Sammensætning, der omfatter HFO-1234ze i en mængde på fra 5 til 99 vægt-% og 1,1,1,2-tetrafluorethan (HFC-134a), hvor sammensætningen har et globalt opvarmningspotentiale (GWP) på højst 1000, fortrinsvis på højst 500, mere fortrinsvis på højst 150, mere fortrinsvis på højst 100, mere fortrinsvis på højst 75.

2. Sammensætning ifølge krav 1, hvor HFO-1234ze er til stede i en mængde på fra 5 vægt-% til 95 vægt-%.

3. Sammensætning ifølge krav 1, hvor HFO-1234ze er trans-HFO-1234ze.

4. Anvendelse af en sammensætning, der omfatter mindst 5 vægt-% HFO-1234ze, og HFC-134a, som et blæsemiddel, hvor sammensætningen har et globalt opvarmningspotentiale (GWP) på højst 1000, fortrinsvis på højst 500, mere fortrinsvis på højst 150, mere fortrinsvis på højst 100, mere fortrinsvis på højst 75.

DRAWINGS

Figure 1