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(54) Benævnelse: **SAMMENSÆTNINGER INDEHOLDENDE DIFLUORMETHAN, TETRAFLUORPROPEN OG CARBONDIOXID OG ANVENDELSER DERAF**

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DESCRIPTION

BACKGROUND

1. Field of the Disclosure.

[0001] The present disclosure relates to compositions for use in air conditioning or heat pump systems. In particular, the compositions of the present invention are useful in methods for producing cooling and heating, and methods for replacing R-32 and air conditioning and heat pump apparatus.

2. Description of Related Art.

[0002] The refrigeration industry has been working for the past few decades to find replacement refrigerants for the ozone-depleting chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) being phased out as a result of the Montreal Protocol. The solution for most refrigerant producers has been the commercialization of hydrofluorocarbon (HFC) refrigerants. These HFC refrigerants, including-134a, R-32 and R-410A, among others, have zero ozone depletion potential and thus are not affected by the current regulatory phase out as a result of the original Montreal Protocol. With implementation to the Kigali amendment to the Montreal Protocol, even lower GWP replacement refrigerants are being sought. US 2015/315446 A1 relates to low GWP heat transfer compositions.

BRIEF SUMMARY

[0003] Certain compositions comprising difluoromethane, tetrafluoropropene and carbon dioxide have been found to possess suitable properties to allow their use as replacements for currently available commercial refrigerants, in particular R-32, with relatively high GWP. Therefore, the present inventors have discovered refrigerant gases that are non-ozone depleting, and have significantly less direct global warming potential than and match the performance of R-32, and are thus, environmentally sustainable alternatives.

[0004] In accordance with the present invention refrigerant compositions are disclosed. The compositions comprise refrigerant mixtures consisting essentially of difluoromethane, tetrafluoropropene and carbon dioxide as defined in claim 1.

[0005] The refrigerant are useful as components in compositions also containing non-refrigerant components (e.g., lubricants and/or additives), in processes to produce cooling or

heating as defined in claims 12 and 13, respectively, in methods for replacing refrigerant R-32 as defined in claim 14, and in air conditioning and heat pump systems as defined in claim 15.

DETAILED DESCRIPTION

[0006] Before addressing details of embodiments described below, some terms are defined or clarified.

Definitions

[0007] As used herein, the term heat transfer fluid (also referred to as heat transfer medium) means a composition used to carry heat from a heat source to a heat sink.

[0008] A heat source is defined as any space, location, object or body from which it is desirable to add, transfer, move or remove heat. Examples of heat sources are spaces (open or enclosed) requiring refrigeration or cooling, such as refrigerator or freezer cases in a supermarket, transport refrigerated containers, building spaces requiring air conditioning, industrial water chillers or the passenger compartment of an automobile requiring air conditioning. In some embodiments, the heat transfer composition may remain in a constant state throughout the transfer process (i.e., not evaporate or condense). In other embodiments, evaporative cooling processes may utilize heat transfer compositions as well.

[0009] A heat sink is defined as any space, location, object or body capable of absorbing heat. A vapor compression refrigeration system is one example of such a heat sink.

[0010] A refrigerant is defined as a heat transfer fluid that undergoes a phase change from liquid to gas and back again during a cycle used to transfer of heat.

[0011] A heat transfer system is the system (or apparatus) used to produce a heating or cooling effect in a particular space. A heat transfer system may be a mobile system or a stationary system.

[0012] Examples of heat transfer systems are any type of refrigeration systems and air conditioning systems including, but are not limited to, stationary heat transfer systems, air conditioners, freezers, refrigerators, heat pumps, water chillers, flooded evaporator chillers, direct expansion chillers, walk-in coolers, mobile refrigerators, mobile heat transfer systems, mobile air conditioning units, dehumidifiers, and combinations thereof.

[0013] Refrigeration capacity (also referred to as cooling capacity) is a term which defines the change in enthalpy of a refrigerant in an evaporator per pound of refrigerant circulated, or the heat removed by the refrigerant in the evaporator per unit volume of refrigerant vapor exiting

the evaporator (volumetric capacity). The refrigeration capacity is a measure of the ability of a refrigerant or heat transfer composition to produce cooling. Therefore, the higher the capacity, the greater the cooling that is produced. Cooling rate refers to the heat removed by the refrigerant in the evaporator per unit time.

[0014] Coefficient of performance (COP) is the amount of heat removed divided by the required energy input to operate the cycle. The higher the COP, the higher is the energy efficiency. COP is directly related to the energy efficiency ratio (EER) that is the efficiency rating for refrigeration or air conditioning equipment at a specific set of internal and external temperatures.

[0015] The term "subcooling" refers to the reduction of the temperature of a liquid below that liquid's saturation point for a given pressure. The saturation point is the temperature at which the vapor is completely condensed to a liquid, but subcooling continues to cool the liquid to a lower temperature liquid at the given pressure. By cooling a liquid below the saturation temperature (or bubble point temperature), the net refrigeration capacity can be increased. Subcooling thereby improves refrigeration capacity and energy efficiency of a system. Subcool amount is the amount of cooling below the saturation temperature (in degrees).

[0016] Superheat is a term that defines how far above its saturation vapor temperature (the temperature at which, if the composition is cooled, the first drop of liquid is formed, also referred to as the "dew point") a vapor composition is heated.

[0017] Temperature glide (sometimes referred to simply as "glide") is the absolute value of the difference between the starting and ending temperatures of a phase-change process by a refrigerant within a component of a refrigerant system, exclusive of any subcooling or superheating. This term may be used to describe condensation or evaporation of a near azeotrope or non-azeotropic composition. When referring to the temperature glide of a refrigeration, air conditioning or heat pump system, it is common to provide the average temperature glide being the average of the temperature glide in the evaporator and the temperature glide in the condenser.

[0018] The net refrigeration effect is the quantity of heat that each kilogram of refrigerant absorbs in the evaporator to produce useful cooling.

[0019] The mass flow rate is the quantity of refrigerant in kilograms circulating through the refrigeration, heat pump or air conditioning system over a given period of time.

[0020] As used herein, the term "lubricant" means any material added to a composition or a compressor (and in contact with any heat transfer composition in use within any heat transfer system) that provides lubrication to the compressor to aid in preventing parts from seizing.

[0021] As used herein, compatibilizers are compounds which improve solubility of the hydrofluorocarbon of the disclosed compositions in heat transfer system lubricants. In some

embodiments, the compatibilizers improve oil return to the compressor. In some embodiments, the composition is used with a system lubricant to reduce oil-rich phase viscosity.

[0022] As used herein, oil-return refers to the ability of a heat transfer composition to carry lubricant through a heat transfer system and return it to the compressor. That is, in use, it is not uncommon for some portion of the compressor lubricant to be carried away by the heat transfer composition from the compressor into the other portions of the system. In such systems, if the lubricant is not efficiently returned to the compressor, the compressor will eventually fail due to lack of lubrication.

[0023] As used herein, "ultra-violet" dye is defined as a UV fluorescent or phosphorescent composition that absorbs light in the ultra-violet or "near" ultra-violet region of the electromagnetic spectrum. The fluorescence produced by the UV fluorescent dye under illumination by a UV light that emits at least some radiation with a wavelength in the range of from 10 nanometers to about 775 nanometers may be detected.

[0024] Flammability is a term used to mean the ability of a composition to ignite and/or propagate a flame. For refrigerants and other heat transfer compositions, the lower flammability limit ("LFL") is the minimum concentration of the heat transfer composition in air that is capable of propagating a flame through a homogeneous mixture of the composition and air under test conditions specified in ASTM (American Society of Testing and Materials) E681. The upper flammability limit ("UFL") is the maximum concentration of the heat transfer composition in air that is capable of propagating a flame through a homogeneous mixture of the composition and air under the same test conditions. Determination of whether a refrigerant compound or mixture is flammable or non-flammable is also done by testing under the conditions of ASTM-681.

[0025] During a refrigerant leak, lower boiling components of a mixture may leak preferentially. Thus, the composition in the system, as well as, the vapor leaking can vary over the time period of the leak. Thus, a non-flammable mixture may become flammable under leakage scenarios. And in order to be classified as non-flammable by ASHRAE (American Society of Heating, Refrigeration and Air-conditioning Engineers), a refrigerant or heat transfer composition must be non-flammable as formulated, but also under leakage conditions.

[0026] Global warming potential (GWP) is an index for estimating relative global warming contribution due to atmospheric emission of a kilogram of a particular greenhouse gas compared to emission of a kilogram of carbon dioxide. GWP can be calculated for different time horizons showing the effect of atmospheric lifetime for a given gas. The GWP for the 100 year time horizon is commonly the value referenced. For mixtures, a weighted average can be calculated based on the individual GWPs for each component.

[0027] Ozone depletion potential (ODP) is a number that refers to the amount of ozone depletion caused by a substance. The ODP is the ratio of the impact on ozone of a chemical compared to the impact of a similar mass of CFC-11 (fluorotrichloromethane). Thus, the ODP

of CFC-11 is defined to be 1.0. Other CFCs and HCFCs have ODPs that range from 0.01 to 1.0. HFCs and HFOs have zero ODP because they do not contain chlorine or other ozone depleting halogens.

[0028] As used herein, the terms "comprises," "comprising," "includes," "including," "has," "having" or any other variation thereof, are intended to cover a non-exclusive inclusion. For example, a composition, process, method, article, or apparatus that comprises a list of elements is not necessarily limited to only those elements but may include other elements not expressly listed or inherent to such composition, process, method, article, or apparatus.

[0029] The transitional phrase "consisting of" excludes any element, step, or ingredient not specified. If in the claim such would close the claim to the inclusion of materials other than those recited except for impurities ordinarily associated therewith. When the phrase "consists of" appears in a clause of the body of a claim, rather than immediately following the preamble, it limits only the element set forth in that clause; other elements are not excluded from the claim as a whole.

[0030] The transitional phrase "consisting essentially of" is used to define a composition, method or apparatus that includes materials, steps, features, components, or elements, in addition to those literally disclosed provided that these additional included materials, steps, features, components, or elements do not materially affect the basic and novel characteristic(s) of the claimed invention. The term 'consisting essentially of occupies a middle ground between "comprising" and 'consisting of. Typically, components of the refrigerant mixtures and the refrigerant mixtures themselves can contain minor amounts (e.g., less than about 0.5 weight percent total) of impurities and/or byproducts (e.g., from the manufacture of the refrigerant components or reclamation of the refrigerant components from other systems) which do not materially affect the novel and basic characteristics of the refrigerant mixture.

[0031] Where applicants have defined an invention or a portion thereof with an open-ended term such as "comprising," it should be readily understood that (unless otherwise stated) the description should be interpreted to also describe such an invention using the terms "consisting essentially of" or "consisting of."

[0032] Also, use of "a" or "an" are employed to describe elements and components described herein. This is done merely for convenience and to give a general sense of the scope of the invention. This description should be read to include one or at least one and the singular also includes the plural unless it is obvious that it is meant otherwise.

[0033] Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of embodiments of the disclosed compositions, suitable methods and materials are described below. All publications, patent applications, patents, and other references mentioned herein are incorporated by reference in their entirety, unless a

particular passage is cited. In case of conflict, the present specification, including definitions, will control. In addition, the materials, methods, and examples are illustrative only and not intended to be limiting.

[0034] 2,3,3,3-tetrafluoropropene may also be referred to as HFO-1234yf, HFC-1234yf, or R-1234yf. HFO-1234yf may be made by methods known in the art, such as by dehydrofluorination 1,1,1,2,3-pentafluoropropane (HFC-245eb) or 1,1,1,2,2-pentafluoropropane (HFC-245cb).

[0035] Difluoromethane (HFC-32 or R-32) is commercially available or may be made by methods known in the art, such as by dechlorofluorination of methylene chloride.

[0036] Carbon dioxide (CO_2) is commercially available from many gas supply houses or may be produced by any of numerous well known methods.

Compositions

[0037] The refrigerants industry has struggled to develop new refrigerant products that provide acceptable performance and environmental sustainability. New global warming regulations may place a cap on global warming potential (GWP) for new refrigerant compositions. Thus, the industry must find, low GWP, low-toxicity, low ozone depletion potential (ODP) compositions that also provide good performance for cooling and heating. Difluoromethane (HFC-32, or R-32) has been found to have desirable properties for a refrigerant or heat transfer composition, but has a moderately high GWP, 675, and therefore, lower GWP replacements for HFC-32 are also being sought.

[0038] In one embodiment, refrigerant mixtures have GWP of 400 or less, based on AR4 data. In another embodiment, refrigerant mixtures have GWP of 300 or less, based on AR4 data.

[0039] The present inventors have identified refrigerant mixtures that provide performance properties to serve as replacements for R-32 in air conditioning and heat pump apparatus. These compositions comprise refrigerant mixtures consisting essentially of difluoromethane, 2,3,3,3-tetrafluoropropene, and carbon dioxide. In one embodiment, the compositions comprising refrigerant mixtures consist of difluoromethane, 2,3,3,3-tetrafluoropropene, and carbon dioxide.

[0040] Identifying replacement refrigerants with the right balance of properties needed by certain applications is not a trivial undertaking. The industry has struggled to find high capacity refrigerants with reasonable temperature glide. In particular, a refrigerant for replacing R-32 that can match the cooling capacity of R-32 with acceptable temperature glide and with GWP of 400 or less, or even 300 or less has been desired.

[0041] Disclosed herein are compositions comprising refrigerant mixtures for replacing R-32

said refrigerant mixtures consisting essentially of from about 42 to about 59 weight percent difluoromethane (HFC-32), about 28 to about 53 weight percent 2,3,3,3-tetrafluoropropene (HFO-1234yf), and about 4 to about 17 weight percent carbon dioxide (CO_2).

[0042] In another embodiment, said refrigerant mixture consists essentially of from about 42 to about 59 weight percent difluoromethane, about 31 to about 49 weight percent 2,3,3,3-tetrafluoropropene, and about 4 to about 17 weight percent carbon dioxide.

[0043] In another embodiment, said refrigerant mixture consists essentially of from about 42 to about 59 weight percent difluoromethane, about 33 to about 48 weight percent 2,3,3,3-tetrafluoropropene, and about 6 to about 15 weight percent carbon dioxide.

[0044] In another embodiment, said refrigerant mixture consists essentially of about 42 to 59 weight percent difluoromethane, about 33 to 46 weight percent 2,3,3,3-tetrafluoropropene, and about 6 to 17 weight percent carbon dioxide.

[0045] In another embodiment, said refrigerant mixture consists essentially of about 47 to 59 weight percent difluoromethane, about 32 to 47 weight percent 2,3,3,3-tetrafluoropropene, and about 8 to 13 weight percent carbon dioxide.

[0046] In another embodiment, said refrigerant mixture consisting essentially of about 47 to 59 weight percent difluoromethane, about 28 to 46 weight percent 2,3,3,3-tetrafluoropropene, and about 4 to 16 weight percent carbon dioxide.

[0047] In another embodiment, said refrigerant mixture consisting essentially of about 47 to 59 weight percent difluoromethane, about 31 to 44 weight percent 2,3,3,3-tetrafluoropropene, and about 6 to 13 weight percent carbon dioxide.

[0048] In another embodiment, said refrigerant mixture consisting essentially of about 47 to 59 weight percent difluoromethane, about 32 to 42 weight percent 2,3,3,3-tetrafluoropropene, and about 8 to 12 weight percent carbon dioxide.

[0049] In another embodiment, said refrigerant mixture consisting essentially of about 42 to 59 weight percent difluoromethane, about 32 to 45 weight percent 2,3,3,3-tetrafluoropropene, and about 6 to 15 weight percent carbon dioxide.

[0050] In another embodiment, said refrigerant mixture consisting essentially of about 44 to 59 weight percent difluoromethane, about 32 to 45 weight percent 2,3,3,3-tetrafluoropropene, and about 6 to 15 weight percent carbon dioxide.

[0051] In another embodiment, said refrigerant mixture consisting essentially of about 44 to 47 weight percent difluoromethane, about 45 to 50 weight percent 2,3,3,3-tetrafluoropropene, and about 6 to 15 weight percent carbon dioxide.

[0052] In another embodiment, said refrigerant mixture consisting essentially of about 42 to 44 weight percent difluoromethane, about 45 to 50 weight percent 2,3,3,3-tetrafluoropropene, and about 6 to 13 weight percent carbon dioxide.

[0053] In another embodiment, said refrigerant mixture consisting essentially of about 42 to 44 weight percent difluoromethane, about 48 to 49 weight percent 2,3,3,3-tetrafluoropropene, and about 7 to 10 weight percent carbon dioxide.

[0054] In another embodiment, said refrigerant mixture consisting essentially of about 43 to 44 weight percent difluoromethane, about 48 to 49 weight percent 2,3,3,3-tetrafluoropropene, and about 6 to 8 weight percent carbon dioxide.

[0055] In another embodiment, said refrigerant mixture consisting essentially of about 44 weight percent difluoromethane, about 49 weight percent 2,3,3,3-tetrafluoropropene, and about 7 weight percent carbon dioxide.

[0056] In another embodiment, said refrigerant mixture consisting essentially of about 43 to 45 weight percent difluoromethane, about 42 to 46 weight percent 2,3,3,3-tetrafluoropropene, and about 9 to 13 weight percent carbon dioxide.

[0057] In another embodiment, said refrigerant mixture consisting essentially of about 43 to 45 weight percent difluoromethane, about 43 to 45 weight percent 2,3,3,3-tetrafluoropropene, and about 11 to 13 weight percent carbon dioxide.

[0058] In another embodiment, said refrigerant mixture consisting essentially of about 44 weight percent difluoromethane, about 44 weight percent 2,3,3,3-tetrafluoropropene, and about 12 weight percent carbon dioxide.

[0059] In another embodiment, said refrigerant mixture consisting essentially of about 44 weight percent difluoromethane, about 43 weight percent 2,3,3,3-tetrafluoropropene, and about 13 weight percent carbon dioxide.

[0060] In another embodiment, said refrigerant mixture consisting essentially of about 55 to 59 weight percent difluoromethane, about 33 to 35 weight percent 2,3,3,3-tetrafluoropropene, and about 7 to 12 weight percent carbon dioxide.

[0061] In another embodiment, said refrigerant mixture consisting essentially of about 57 to 59 weight percent difluoromethane, about 33 to 34 weight percent 2,3,3,3-tetrafluoropropene, and about 7 to 9 weight percent carbon dioxide.

[0062] In another embodiment, said refrigerant mixture consisting essentially of about 58 weight percent difluoromethane, about 34 weight percent 2,3,3,3-tetrafluoropropene, and about 8 weight percent carbon dioxide.

[0063] In another embodiment, said refrigerant mixture consisting essentially of about 58 weight percent difluoromethane, about 33 weight percent 2,3,3,3-tetrafluoropropene, and about 9 weight percent carbon dioxide.

[0064] In any of the above embodiment, the total of the refrigerant mixture, must add to 100%.

[0065] In one embodiment, the refrigerant mixtures provide replacements for R-32 with cooling capacity within 10% of the cooling capacity for R-32. In another embodiment, the refrigerant mixtures provide replacements for R-32 with cooling capacity within 5% of the cooling capacity for R-32. In another embodiment, the refrigerant mixtures provide replacements for R-32 with cooling capacity within 2% of the cooling capacity for R-32. In another embodiment, the refrigerant mixtures provide replacements for R-32 with cooling capacity that matches or improves upon the cooling capacity for R-32.

[0066] Of particular interest, as replacements for R-32, are compositions as listed in Table A.
Table A

R32/R1234yf/CO_2 (wt%)	
	44/49/7
59/37/4	44/48/8
59/36/5	44/47/9
59/35/6	44/46/10
59/34/7	44/45/11
59/33/8	44/44/12
59/32/9	44/43/13
59/31/10	44/42/14
59/30/11	44/41/15
59/29/12	44/40/16
59/28/13	44/39/17
58/38/4	43/48/9
58/37/5	43/47/10
58/36/6	43/46/11
58/35/7	43/45/12
58/34/8	43/44/13
58/33/9	43/43/14
58/32/10	43/42/15
58/31/11	43/41/16
47/47/6	43/40/17
47/46/7	42/49/9

R32/R1234yf/CO_2 (wt%)	
47/45/8	42/48/10
47/44/9	42/47/11
47/43/10	42/46/12
47/42/11	42/45/13
47/41/12	42/44/14
47/40/13	42/43/15
47/39/14	42/42/16
47/38/15	42/41/17
47/39/16	48/45/7
49/44/7	52/41/7
50/43/7	53/40/7
51/42/7	54/38/8
55/37/8	57/35/8
56/36/8	57/36/7

[0067] In some embodiments, in addition to the difluoromethane, 2,3,3,3-tetrafluoropropene, and carbon dioxide, the disclosed compositions may comprise optional non-refrigerant components. Thus, disclosed herein are compositions comprising a refrigerant mixture consisting essentially of difluoromethane, 2,3,3,3-tetrafluoropropene, and carbon dioxide, further comprising one or more optional non-refrigerant components selected from the group consisting of lubricants, dyes (including UV dyes), solubilizing agents, compatibilizers, stabilizers, tracers, anti-wear agents, extreme pressure agents, corrosion and oxidation inhibitors, metal surface energy reducers, metal surface deactivators, free radical scavengers, foam control agents, viscosity index improvers, pour point depressants, detergents, viscosity adjusters, and mixtures thereof. In some embodiments, the optional non-refrigerant components may be referred to as additives. Indeed, many of these optional non-refrigerant components fit into one or more of these categories and may have qualities that lend themselves to achieve one or more performance characteristic.

[0068] In some embodiments, one or more non-refrigerant components are present in small amounts relative to the overall composition. In some embodiments, the amount of additive(s) concentration in the disclosed compositions is from less than about 0.1 weight percent to as much as about 5 weight percent of the total composition. In some embodiments of the present invention, the additives are present in the disclosed compositions in an amount between about 0.1 weight percent to about 5 weight percent of the total composition or in an amount between about 0.1 weight percent to about 3.5 weight percent. The additive component(s) selected for the disclosed composition is selected on the basis of the utility and/or individual equipment components or the system requirements.

[0069] In one embodiment, the lubricant is selected from the group consisting of mineral oil, alkylbenzene, polyol esters, polyalkylene glycols, polyvinyl ethers, polycarbonates, perfluoropolyethers, silicones, silicate esters, phosphate esters, paraffins, naphthenes, polyalpha-olefins, and combinations thereof.

[0070] The lubricants as disclosed herein may be commercially available lubricants. For instance, the lubricant may be paraffinic mineral oil, sold by BVA Oils as BVM 100 N, naphthenic mineral oils sold by Crompton Co. under the trademarks Suniso® 1GS, Suniso® 3GS and Suniso® 5GS, naphthenic mineral oil sold by Pennzoil under the trademark Sontex® 372LT, naphthenic mineral oil sold by Calumet Lubricants under the trademark Calumet® RO-30,, linear alkylbenzenes sold by Shrieve Chemicals under the trademarks Zerol® 75, Zerol® 150 and Zerol® 500 and branched alkylbenzene sold by Nippon Oil as HAB 22, polyol esters (POEs) sold under the trademark Castrol® 100 by Castrol, United Kingdom, polyalkylene glycols (PAGs) such as RL-488A from Dow (Dow Chemical, Midland, Michigan), and mixtures thereof, meaning mixtures of any of the lubricants disclosed in this paragraph.

[0071] In the compositions of the present invention including a lubricant, the lubricant is present in an amount of less than 40.0 weight percent to the total composition. In other embodiments, the amount of lubricant is less than 20 weight percent of the total composition. In other embodiments, the amount of lubricant is less than 10 weight percent of the total composition. In other embodiments, the about of lubricant is between about 0.1 and 5.0 weight percent of the total composition.

[0072] Notwithstanding the above weight ratios for compositions disclosed herein, it is understood that in some heat transfer systems, while the composition is being used, it may acquire additional lubricant from one or more equipment components of such heat transfer system. For example, in some refrigeration, air conditioning and heat pump systems, lubricants may be charged in the compressor and/or the compressor lubricant sump. Such lubricant would be in addition to any lubricant additive present in the refrigerant in such a system. In use, the refrigerant composition when in the compressor may pick up an amount of the equipment lubricant to change the refrigerant-lubricant composition from the starting ratio.

[0073] The non-refrigerant component used with the compositions of the present invention may include at least one dye. The dye may be at least one ultra-violet (UV) dye. The UV dye may be a fluorescent dye. The fluorescent dye may be selected from the group consisting of naphthalimides, perylenes, coumarins, anthracenes, phenanthracenes, xanthenes, thioxanthenes, naphthoxanthenes, fluoresceins, and derivatives of said dye, and combinations thereof, meaning mixtures of any of the foregoing dyes or their derivatives disclosed in this paragraph.

[0074] In some embodiments, the disclosed compositions contain from about 0.001 weight percent to about 1.0 weight percent UV dye. In other embodiments, the UV dye is present in an

amount of from about 0.005 weight percent to about 0.5 weight percent; and in other embodiments, the UV dye is present in an amount of from 0.01 weight percent to about 0.25 weight percent of the total composition.

[0075] UV dye is a useful component for detecting leaks of the composition by permitting one to observe the fluorescence of the dye at or in the vicinity of a leak point in an apparatus (e.g., refrigeration unit, air-conditioner or heat pump). The UV emission, e.g., fluorescence from the dye may be observed under an ultra-violet light. Therefore, if a composition containing such a UV dye is leaking from a given point in an apparatus, the fluorescence can be detected at the leak point, or in the vicinity of the leak point.

[0076] Another non-refrigerant component which may be used with the compositions of the present invention may include at least one solubilizing agent selected to improve the solubility of one or more dye in the disclosed compositions. In some embodiments, the weight ratio of dye to solubilizing agent ranges from about 99:1 to about 1:1. The solubilizing agents include at least one compound selected from the group consisting of hydrocarbons, hydrocarbon ethers, polyoxyalkylene glycol ethers (such as dipropylene glycol dimethyl ether), amides, nitriles, ketones, chlorocarbons (such as methylene chloride, trichloroethylene, chloroform, or mixtures thereof), esters, lactones, aromatic ethers, fluoroethers and 1,1,1-trifluoroalkanes and mixtures thereof, meaning mixtures of any of the solubilizing agents disclosed in this paragraph.

[0077] In some embodiments, the non-refrigerant component comprises at least one compatibilizer to improve the compatibility of one or more lubricants with the disclosed compositions. The compatibilizer may be selected from the group consisting of hydrocarbons, hydrocarbon ethers, polyoxyalkylene glycol ethers (such as dipropylene glycol dimethyl ether), amides, nitriles, ketones, chlorocarbons (such as methylene chloride, trichloroethylene, chloroform, or mixtures thereof), esters, lactones, aromatic ethers, fluoroethers, 1,1,1-trifluoroalkanes, and mixtures thereof, meaning mixtures of any of the compatibilizers disclosed in this paragraph.

[0078] The solubilizing agent and/or compatibilizer may be selected from the group consisting of hydrocarbon ethers consisting of the ethers containing only carbon, hydrogen and oxygen, such as dimethyl ether (DME) and mixtures thereof, meaning mixtures of any of the hydrocarbon ethers disclosed in this paragraph.

[0079] The compatibilizer may be linear or cyclic aliphatic or aromatic hydrocarbon compatibilizer containing from 3 to 15 carbon atoms. The compatibilizer may be at least one hydrocarbon, which may be selected from the group consisting of at least propanes, including propylene and propane, butanes, including n-butane and isobutene, pentanes, including n-pentane, isopentane, neopentane and cyclopentane, hexanes, octanes, nonane, and decanes, among others. Commercially available hydrocarbon compatibilizers include but are not limited to those from Exxon Chemical (USA) sold under the trademarks Isopar® H, a mixture of undecane (C_{11}) and dodecane (C_{12}) (a high purity C_{11} to C_{12} isoparaffinic), Aromatic 150 (a C_9

to C_{11} aromatic), Aromatic 200 (a C_9 to C_{15} aromatic) and Naptha 140 (a mixture of C_5 to C_{11} paraffins, naphthenes and aromatic hydrocarbons) and mixtures thereof, meaning mixtures of any of the hydrocarbons disclosed in this paragraph.

[0080] The compatibilizer may alternatively be at least one polymeric compatibilizer. The polymeric compatibilizer may be a random copolymer of fluorinated and non-fluorinated acrylates, wherein the polymer comprises repeating units of at least one monomer represented by the formulae $CH_2=C(R^1)CO_2R^2$, $CH_2=C(R^3)C_6H_4R^4$, and $CH_2=C(R^5)C_6H_4XR^6$, wherein X is oxygen or sulfur; R^1, R^3, and R^5 are independently selected from the group consisting of H and C_1-C_4 alkyl radicals; and R^2, R^4, and R^6 are independently selected from the group consisting of carbon-chain-based radicals containing C, and F, and may further contain H, Cl, ether oxygen, or sulfur in the form of thioether, sulfoxide, or sulfone groups and mixtures thereof. Examples of such polymeric compatibilizers include those commercially available from E. I. du Pont de Nemours and Company, (Wilmington, DE, 19898, USA) under the trademark Zonyl®® PHS. Zonyl® PHS is a random copolymer made by polymerizing 40 weight percent $CH_2=C(CH_3)CO_2CH_2CH_2(CF_2CF_2)_mF$ (also referred to as Zonyl®® fluoromethacrylate or ZFM) wherein m is from 1 to 12, primarily 2 to 8, and 60 weight percent lauryl methacrylate ($CH_2=C(CH_3)CO_2(CH_2)_{11}CH_3$, also referred to as LMA).

[0081] In some embodiments, the compatibilizer component contains from about 0.01 to 30 weight percent (based on total amount of compatibilizer) of an additive which reduces the surface energy of metallic copper, aluminum, steel, or other metals and metal alloys thereof found in heat exchangers in a way that reduces the adhesion of lubricants to the metal. Examples of metal surface energy reducing additives include those commercially available from DuPont under the trademarks Zonyl® FSA, Zonyl® FSP, and Zonyl® FSJ.

[0082] Another optional non-refrigerant component which may be used with the compositions of the present invention may be a metal surface deactivator. The metal surface deactivator is selected from the group consisting of areoxalyl bis (benzylidene) hydrazide (CAS reg no. 6629-10-3), N,N'-bis(3,5-di-tert-butyl-4-hydroxyhydrocinnamoylhydrazine (CAS reg no. 32687-78-8) , 2,2,' - oxamidobis-ethyl-(3,5-di-tert-butyl-4-hydroxyhydrocinnamate (CAS reg no. 70331-94-1), N,N'-(disalicyclidene)-1,2-diaminopropane (CAS reg no. 94-91-7) and ethylenediaminetetra-acetic acid (CAS reg no. 60-00-4) and its salts, and mixtures thereof, meaning mixtures of any of the metal surface deactivators disclosed in this paragraph.

[0083] The optional non-refrigerant component used with the compositions of the present invention may alternatively be a stabilizer selected from the group consisting of hindered phenols, thiophosphates, butylated triphenylphosphorothionates, organo phosphates, or phosphites, aryl alkyl ethers, terpenes, terpenoids, epoxides, fluorinated epoxides, oxetanes, ascorbic acid, thiols, lactones, thioethers, amines, nitromethane, alkylsilanes, benzophenone derivatives, aryl sulfides, divinyl terephthalic acid, diphenyl terephthalic acid, ionic liquids, and mixtures thereof, meaning mixtures of any of the stabilizers disclosed in this paragraph.

[0084] The stabilizer may be selected from the group consisting of tocopherol; hydroquinone; t-butyl hydroquinone; monothiophosphates; and dithiophosphates, commercially available from Ciba Specialty Chemicals, Basel, Switzerland, hereinafter "Ciba", under the trademark Irgalube® 63; dialkylthiophosphate esters, commercially available from Ciba under the trademarks Irgalube® 353 and Irgalube® 350, respectively; butylated triphenylphosphorothionates, commercially available from Ciba under the trademark Irgalube® 232; amine phosphates, commercially available from Ciba under the trademark Irgalube® 349 (Ciba); hindered phosphites, commercially available from Ciba as Irgafos® 168 and Tris-(di-tert-butylphenyl)phosphite, commercially available from Ciba under the trademark Irgafos® OPH; (Di-n-octyl phosphite); and iso-decyl diphenyl phosphite, commercially available from Ciba under the trademark Irgafos® DDPP; trialkyl phosphates, such as trimethyl phosphate, triethylphosphate, tributyl phosphate, trioctyl phosphate, and tri(2-ethylhexyl)phosphate; triaryl phosphates including triphenyl phosphate, tricresyl phosphate, and trixylenyl phosphate; and mixed alkyl-aryl phosphates including isopropylphenyl phosphate (IPPP), and bis(t-butylphenyl)phenyl phosphate (TBPP); butylated triphenyl phosphates, such as those commercially available under the trademark Syn-O-Ad® including Syn-O-Ad® 8784; tert-butylated triphenyl phosphates such as those commercially available under the trademark Durad®620; isopropylated triphenyl phosphates such as those commercially available under the trademarks Durad® 220 and Durad®110; anisole; 1,4-dimethoxybenzene; 1,4-diethoxybenzene; 1,3,5-trimethoxybenzene; myrcene, alloocimene, limonene (in particular, d-limonene); retinal; pinene; menthol; geraniol; farnesol; phytol; Vitamin A; terpinene; delta-3-carene; terpinolene; phellandrene; fenchene; dipentene; caratenoids, such as lycopene, beta carotene, and xanthophylls, such as zeaxanthin; retinoids, such as hepaxanthin and isotretinoin; bornane; 1,2-propylene oxide; 1,2-butylene oxide; n-butyl glycidyl ether; trifluoromethyloxirane; 1,1-bis(trifluoromethyl)oxirane; 3-ethyl-3-hydroxymethyl-oxetane, such as OXT-101 (Toagosei Co., Ltd); 3-ethyl-3-((phenoxy)methyl)-oxetane, such as OXT-211 (Toagosei Co., Ltd); 3-ethyl-3-((2-ethyl-hexyloxy)methyl)-oxetane, such as OXT-212 (Toagosei Co., Ltd); ascorbic acid; methanethiol (methyl mercaptan); ethanethiol (ethyl mercaptan); Coenzyme A; dimercaptosuccinic acid (DMSA); grapefruit mercaptan ((R)-2-(4-methylcyclohex-3-enyl)propane-2-thiol)); cysteine ((R)-2-amino-3-sulfanyl-propanoic acid); lipoamide (1,2-dithiolane-3-pentanamide); 5,7-bis(1,1-dimethylethyl)-3-[2,3(or 3,4)-dimethylphenyl]-2(3H)-benzofuranone, commercially available from Ciba under the trademark Irganox® HP-136; benzyl phenyl sulfide; diphenyl sulfide; diisopropylamine; dioctadecyl 3,3'-thiodipropionate, commercially available from Ciba under the trademark Irganox® PS 802 (Ciba); didodecyl 3,3'-thiopropionate, commercially available from Ciba under the trademark Irganox® PS 800; di-(2,2,6,6-tetramethyl-4-piperidyl)sebacate, commercially available from Ciba under the trademark Tinuvin® 770; poly-(N-hydroxyethyl-2,2,6,6-tetramethyl-4-hydroxy-piperidyl succinate, commercially available from Ciba under the trademark Tinuvin® 622LD (Ciba); methyl bis tallow amine; bis tallow amine; phenol-alpha-naphthylamine;

bis(dimethylamino)methylsilane (DMAMS); tris(trimethylsilyl)silane (TTMSS); vinyltriethoxysilane; vinyltrimethoxysilane; 2,5-difluorobenzophenone; 2',5'-dihydroxyacetophenone; 2-aminobenzophenone; 2-chlorobenzophenone; benzyl phenyl sulfide; diphenyl sulfide; dibenzyl sulfide; ionic liquids; and mixtures and combinations thereof.

[0085] The optional non-refrigerant component used with the compositions of the present invention may alternatively be an ionic liquid stabilizer. The ionic liquid stabilizer may be selected from the group consisting of organic salts that are liquid at room temperature (approximately 25 °C), those salts containing cations selected from the group consisting of pyridinium, pyridazinium, pyrimidinium, pyrazinium, imidazolium, pyrazolium, thiazolium, oxazolium and triazolium and mixtures thereof; and anions selected from the group consisting of $[BF_4]$-, $[PF_6]$-, $[SbF_6]$-, $[CF_3SO_3]$-, $[HCF_2CF_2SO_3]$-, $[CF_3HFCCF_2SO_3]$-, $[HCClFCF_2SO_3]$-, $[(CF_3SO_2)_2N]$-, $[(CF_3CF_2SO_2)_2N]$-, $[(CF_3SO_2)_3C]$-, $[CF_3CO_2]$-, and F- and mixtures thereof. In some embodiments, ionic liquid stabilizers are selected from the group consisting of emim BF_4 (1-ethyl-3-methylimidazolium tetrafluoroborate); bmim BF_4 (1-butyl-3-methylimidazolium tetraborate); emim PF_6 (1-ethyl-3-methylimidazolium hexafluorophosphate); and bmim PF_6 (1-butyl-3-methylimidazolium hexafluorophosphate), all of which are available from Fluka (Sigma-Aldrich).

[0086] In some embodiments, the stabilizer may be a hindered phenol, which is any substituted phenol compound, including phenols comprising one or more substituted or cyclic, straight chain, or branched aliphatic substituent group, such as, alkylated monophenols including 2,6-di-tert-butyl-4-methylphenol; 2,6-di-tert-butyl-4-ethylphenol; 2,4-dimethyl-6-tertbutylphenol; tocopherol; and the like, hydroquinone and alkylated hydroquinones including t-butyl hydroquinone, other derivatives of hydroquinone; and the like, hydroxylated thiodiphenyl ethers, including 4,4'-thio-bis(2-methyl-6-tert-butylphenol); 4,4'-thiobis(3-methyl-6-tertbutylphenol); 2,2'-thiobis(4methyl-6-tert-butylphenol); and the like, alkylidene-bisphenols including,: 4,4'-methylenebis(2,6-di-tert-butylphenol); 4,4'-bis(2,6-di-tert-butylphenol); derivatives of 2,2'- or 4,4-biphenoldiols; 2,2'-methylenebis(4-ethyl-6-tertbutylphenol); 2,2'-methylenebis(4-methyl-6-tertbutylphenol); 4,4-butylidenebis(3-methyl-6-tert-butylphenol); 4,4-isopropylidenebis(2,6-di-tertbutylphenol); 2,2'-methylenebis(4-methyl-6-nonylphenol); 2,2'-isobutylidenebis(4,6-dimethylphenol; 2,2'-methylenebis(4-methyl-6-cyclohexylphenol, 2,2- or 4,4- biphenyldiols including 2,2'-methylenebis(4-ethyl-6-tert-butylphenol); butylated hydroxytoluene (BHT, or 2,6-di-tert-butyl-4-methylphenol), bisphenols comprising heteroatoms including 2,6-di-tert-alpha-dimethylamino-p-cresol, 4,4-thiobis(6-tert-butyl-m-cresol); and the like; acylaminophenols; 2,6-di-tert-butyl-4(N,N'-dimethylaminomethylphenol); sulfides including; bis(3-methyl-4-hydroxy-5-tert-butylbenzyl)sulfide; bis(3,5-di-tert-butyl-4-hydroxybenzyl)sulfide and mixtures thereof, meaning mixtures of any of the phenols disclosed in this paragraph.

[0087] In some embodiments, a stabilizer may be a single stabilizing compound as described in detail above. In other embodiments, a stabilizer may be a mixture of two or more of the stabilizing compounds, either from the same class of compounds or from differing classes of compounds, said classes being described in detail above.

[0088] The optional non-refrigerant component, which is used with compositions of the present invention, may alternatively be a tracer. The tracer may be two or more tracer compounds from the same class of compounds or from different classes of compounds. In some embodiments, the tracer is present in the compositions at a total concentration of about 1 part per million by weight (ppm) to about 5000 ppm, based on the weight of the total composition. In other embodiments, the tracer is present at a total concentration of about 10 ppm to about 1000 ppm. In other embodiments, the tracer is present at a total concentration of about 20 ppm to about 500 ppm. In other embodiments, the tracer is present at a total concentration of about 25 ppm to about 500 ppm. In other embodiments, the tracer is present at a total concentration of about 50 ppm to about 500 ppm. Alternatively, the tracer is present at a total concentration of about 100 ppm to about 300 ppm.

[0089] The tracer may be selected from the group consisting of hydrofluorocarbons (HFCs), deuterated hydrofluorocarbons, chlorofluororcarbons (CFCs), hydrofluorochlorocarbons (HCFCs), chlorocarbons, perfluorocarbons, fluoroethers, brominated compounds, iodated compounds, alcohols, aldehydes and ketones, nitrous oxide and combinations thereof. Alternatively, the tracer may be selected from the group consisting of trifluoromethane (HFC-23), dichlorodifluoromethane (CFC-12), chlorodifluoromethane HCFC-22), methyl chloride (R-40), chlorofluoromethane (HCFC-31), fluoroethane (HFC-161), 1,1,-difluoroethane (HFC-152a), 1,1,1-trifluoroethane (HFC-143a), chloropentafluoroethane (CFC-115), 1,2-dichloro-1,1,2,2-tetrafluoroethane (CFC-114), 1,1 -dichloro-1,2,2,2-tetrafluoroethane (CFC-114a), 2-chloro-1,1,1,2-tetrafluoroethane (HCFC-124), pentafluoroethane (HFC-125), 1,1,2,2-tetrafluoroethane (HFC-134), 1,1,1,2-tetrafluoroethane (HFC-134a), 1,1,1,3,3,3-hexafluoropropane (HFC-236fa), 1,1,1,2,3,3,3-heptafluoropropane (HFC-227ea), 1,1,1,2,2,3,3- heptafluoropropane (HFC-227ea), 1,1,1,3,3-pentafluoropropane(HFC-245fa), 1,1,1,2,2-pentafluoropropane (HFC-245cb), 1,1,1,2,3-pentafluoropropane (HFC-245eb), 1,1,2,2-tetrafluoropropane (HFC-254cb), 1,1,1,2-tetrafluoropropane (HFC-254eb), 1,1,1-trifluoropropane (HFC-263fb), 1,1-difluoro-2-chloroethylene (HCFC-1122), 2-chloro-1,1,2-trifluoroethylene (CFC-1113), 1,1,1,3,3-pentafluorobutane (HFC-365mfc), 1,1,1,2,3,4,4,5,5,5-decafluoropentane (HFC-43-10mee), 1,1,1,2,2,3,4,5,5,6,6,7,7,7-tetradecafluoroheptane, hexafluorobutadiene, 3,3,3-trifluoropropyne, iodotrifluoromethane, deuterated hydrocarbons, deuterated hydrofluorocarbons, perfluorocarbons, fluoroethers, brominated compounds, iodated compounds, alcohols, aldehydes, ketones, nitrous oxide (N_2O) and mixtures thereof. In some embodiments, the tracer is a blend containing two or more hydrofluorocarbons, or one hydrofluorocarbon in combination with one or more perfluorocarbons. In other embodiments, the tracer is a blend of at least one CFC and at least one HCFC.

[0090] The tracer may be added to the compositions of the present invention in predetermined quantities to allow detection of any dilution, contamination or other alteration of the composition. Additionally, the tracers may allow detection of product that infringes existing patent rights, by identification of the patent owner's product versus competitive infringing product. Further, in one embodiment, the tracer compounds may allow detection of a manufacturing process by which a product is produced, thus, allowing detection of infringement

of a patent to specific manufacturing process chemistry.

[0091] The additive which may be used with the compositions of the present invention may alternatively be a perfluoropolyether as described in detail in US2007-0284555, incorporated herein by reference.

[0092] It will be recognized that certain of the additives referenced above as suitable for the non-refrigerant component have been identified as potential refrigerants. However, in accordance with this invention, when these additives are used, they are not present at an amount that would affect the novel and basic characteristics of the refrigerant mixtures of this invention. Preferably, the refrigerant mixtures and the compositions of this invention containing them, contain no more than about 0.5 weight percent of the refrigerants other than HFC-32, HFO-1234yf, and CO_2.

[0093] In one embodiment, the compositions disclosed herein may be prepared by any convenient method to combine the desired amounts of the individual components. A preferred method is to weigh the desired component amounts and thereafter combine the components in an appropriate vessel. Agitation may be used, if desired.

[0094] Compositions of the present invention have zero ozone depletion potential and low global warming potential (GWP). Additionally, the compositions of the present invention will have global warming potentials that are less than many hydrofluorocarbon refrigerants currently in use.

Apparatus and Methods of Use

[0095] The compositions disclosed herein are useful as heat transfer compositions or refrigerants. In particular, the compositions comprising HFC-32, HFO-1234yf, and CO_2 are useful as refrigerants. Also, the compositions comprising HFC-32, HFO-1234yf, and CO_2 are useful as replacements for or R-410A in refrigeration, air conditioning or heat pump systems. In particular, the compositions comprising a refrigerant mixture consisting essentially of HFC-32, HFO-1234yf, and CO_2 are useful as replacements for R-32 in air conditioning and heat pump systems and apparatus. Alternatively, the compositions comprising a refrigerant mixture consisting of HFC-32, HFO-1234yf, and CO_2 are useful as replacements for R-32 in air conditioning and heat pump systems and apparatus.

[0096] Thus, disclosed herein is a process for producing cooling comprising evaporating a composition comprising a refrigerant mixture consisting essentially of HFC-32, HFO-1234yf, and CO_2, in the vicinity of a body to be cooled, and thereafter condensing said composition. Alternatively, the process for producing cooling comprises evaporating a composition comprising a refrigerant mixture consisting of HFC-32, HFO-1234yf, and CO_2 in the vicinity of a body to be cooled and thereafter condensing said composition.

[0097] In another embodiment, disclosed herein is a process for producing heating comprising evaporating a composition comprising a refrigerant mixture consisting essentially of HFC-32, HFO-1234yf, and CO_2 and thereafter condensing said composition in the vicinity of a body to be heated. Alternatively, the process for producing heating comprises evaporating a composition comprising a refrigerant mixture consisting of HFC-32, HFO-1234yf, and CO_2 and thereafter condensing said composition in the vicinity of a body to be heated

[0098] Vapor-compression refrigeration, air conditioning and heat pump systems include an evaporator, a compressor, a condenser, and an expansion device. A refrigeration cycle re-uses refrigerant in multiple steps producing a cooling effect in one step and a heating effect in a different step. The cycle can be described simply as follows. Liquid refrigerant enters an evaporator through an expansion device, and the liquid refrigerant boils in the evaporator, by withdrawing heat from the environment, at a low temperature to form a gas and produce cooling. Often air or a heat transfer fluid flows over or around the evaporator to transfer the cooling effect caused by the evaporation of the refrigerant in the evaporator to a body to be cooled. The low-pressure gas enters a compressor where the gas is compressed to raise its pressure and temperature. The higher-pressure (compressed) gaseous refrigerant then enters the condenser in which the refrigerant condenses and discharges its heat to the environment. The refrigerant returns to the expansion device through which the liquid expands from the higher-pressure level in the condenser to the low-pressure level in the evaporator, thus repeating the cycle.

[0099] A body to be cooled or heated may be defined as any space, location, object or body for which it is desirable to provide cooling or heating. Examples include spaces (open or enclosed) requiring air conditioning, cooling, or heating, such as a room, an apartment, or building, such as an apartment building, university dormitory, townhouse, or other attached house or single family home, hospitals, office buildings, supermarkets, college or university classrooms or administration buildings and automobile or truck passenger compartments.

[0100] By "in the vicinity of" is meant that the evaporator of the system containing the refrigerant composition is located either within or adjacent to the body to be cooled, such that air moving over the evaporator would move into or around the body to be cooled. In the process for producing heating, "in the vicinity of" means that the condenser of the system containing the refrigerant composition is located either within or adjacent to the body to be heated, such that the air moving over the evaporator would move into or around the body to be heated.

[0101] A method is provided for replacing R-32 in air conditioning or heat pump systems comprising replacing said R-32 with a composition comprising a refrigerant, air conditioning or heat pump system in place of R-32. Alternatively, the method for replacing R-32 in air conditioning or heat pump systems comprises replacing said R-32 with a composition comprising a refrigerant mixture consisting of HFC-32, HFO-1234yf, and CO_2 to said air conditioning or heat pump system in place of R-32.

[0102] Often replacement refrigerants are most useful if capable of being used in the original refrigeration equipment designed for a different refrigerant. Additionally, the compositions as disclosed herein may be useful as replacements for R-32 in equipment designed for R-32 with minimal to no system modifications. Further, the compositions may be useful for replacing R-32 in equipment specifically modified for or produced entirely for these new compositions comprising HFC-32, HFO-1234yf, and CO_2.

[0103] In many applications, some embodiments of the disclosed compositions are useful as refrigerants and provide at least comparable cooling performance (meaning cooling capacity) as the refrigerant for which a replacement is being sought.

[0104] In one embodiment is provided a method for replacing R-32 comprising charging an air conditioning or heat pump system with a composition comprising HFC-32, HFO-1234yf, and CO_2 as replacement for said R-32.

[0105] In one embodiment of the method, the cooling capacity provided by the composition comprising a refrigerant mixture consisting essentially of HFC-32, HFO-1234yf, and CO_2 is within about ±10% of that produced by R-32 under the same operating conditions. In another embodiment of the method, the cooling capacity provided by the composition comprising a refrigerant mixture consisting essentially of HFC-32, HFO-1234yf, and CO_2 is within about ±5% of that produced by R-32 under the same operating conditions. In another embodiment of the method, the cooling capacity provided by the composition comprising a refrigerant mixture consisting essentially of HFC-32, HFO-1234yf, and CO_2 is within about ±2% of that produced by R-32 under the same operating conditions.

[0106] Additionally, disclosed herein is an air conditioning or heat pump system comprising an evaporator, compressor, condenser and an expansion device characterized by containing a composition comprising HFC-32, HFO-1234yf, and CO_2.

[0107] It has been found that the compositions of the present invention will have some temperature glide in the heat exchangers. Thus, the systems will operate more efficiently if the heat exchangers are operated in counter-current mode or cross-current mode with counter-current tendency. Counter-current tendency means that the closer the heat exchanger can get to counter-current mode the more efficient the heat transfer. Thus, air conditioning heat exchangers, in particular, evaporators, are designed to provide some aspect of counter-current tendency. Therefore, provided herein is an air conditioning or heat pump system wherein said system includes one or more heat exchangers (either evaporators, condensers or both) that operate in counter-current mode or cross-current mode with counter-current tendency.

[0108] Additionally, the compositions of the present invention can be used in systems with heat exchangers operating in cross-current mode.

[0109] In another embodiment, provided herein is a refrigeration system wherein said system includes one or more heat exchangers (either evaporators, condensers or both) that operate in counter-current mode, cross-current mode, or cross-current mode with counter-current tendency.

[0110] In one embodiment, the refrigeration, air conditioning or heat pump system is a stationary refrigeration, air conditioning or heat pump system. In another embodiment the refrigeration, air conditioning or heat pump system is a mobile refrigeration, air conditioning or heat pump system.

[0111] Additionally, in some embodiments, the disclosed compositions may function as primary refrigerants in secondary loop systems that provide cooling to remote locations by use of a secondary heat transfer fluid, which may comprise water, an aqueous salt solution (e.g., calcium chloride), a glycol, carbon dioxide, or a fluorinated hydrocarbon fluid. In this case the secondary heat transfer fluid is the body to be cooled as it is adjacent to the evaporator and is cooled before moving to a second remote body to be cooled.

[0112] Examples of air conditioning or heat pump systems include but are not limited to air conditioners, residential heat pumps, chillers, including flooded evaporator chillers and direct expansion chillers, mobile air conditioning units, dehumidifiers, and combinations thereof.

[0113] As used herein, mobile refrigeration, air conditioning or heat pump systems refers to any refrigeration, air conditioner or heat pump apparatus incorporated into a transportation unit for the road, rail, sea or air. Mobile air conditioning or heat pumps systems may be used in automobiles, trucks, railcars or other transportation systems. Mobile refrigeration may include transport refrigeration in trucks, airplanes, or rail cars. In addition, apparatus which are meant to provide refrigeration for a system independent of any moving carrier, known as "intermodal" systems, are including in the present inventions. Such intermodal systems include "containers" (combined sea/land transport) as well as "swap bodies" (combined road and rail transport).

[0114] As used herein, stationary air conditioning or heat pump systems are systems that are fixed in place during operation. A stationary air conditioning or heat pump system may be associated within or attached to buildings of any variety. These stationary applications may be stationary air conditioning and heat pumps, including but not limited to chillers, heat pumps, including residential and high temperature heat pumps, residential, commercial or industrial air conditioning systems, and including window, ductless, ducted, packaged terminal, and those exterior but connected to the building such as rooftop systems.

[0115] Examples of refrigeration systems the disclosed compositions may be useful in are equipment including commercial, industrial or residential refrigerators and freezers, ice machines, self-contained coolers and freezers, flooded evaporator chillers, direct expansion chillers, walk-in and reach-in coolers and freezers, and combination systems. In some embodiments, the disclosed compositions may be used in supermarket refrigeration systems. Additionally, stationary applications may utilize a secondary loop system that uses a primary

refrigerant to produce cooling in one location that is transferred to a remote location via a secondary heat transfer fluid.

[0116] In the air conditioning and heat pump system of the present invention, the heat exchangers will operate within certain temperature limitations. For air conditioning, in one embodiment, the evaporator will operate at midpoint temperature of about 0°C to about 20°C. In another embodiment, the evaporator will operate at midpoint temperature of about 0°C to about 15°C. In yet another embodiment, the evaporator will operate at midpoint temperature of about 5°C to about 10°C. In one embodiment, the condenser will operate at midpoint temperature of about 15°C to about 60°C. In another embodiment, the condenser will operate at midpoint temperature of about 20°C to about 60°C.

EXAMPLES

[0117] The concepts disclosed herein will be further described in the following examples, which do not limit the scope of the invention described in the claims.

EXAMPLE

Cooling Performance

[0118] Cooling performance at typical conditions for air conditioning and heat pump apparatus for compositions of the present invention is determined and displayed in Table 1 as compared to R-32. The GWP values are from the Intergovernmental Panel on Climate Change (IPCC) Fourth Assessment Report, Working Group I, 2007 (AR4). Average temperature glide (Average Temp Glide: the average of the temperature glide in the evaporator and the temperature glide in the condenser), cooling capacity (Capacity), and compressor discharge temperatures (Compr Disch Temp) are calculated from physical property measurements for the compositions of the present invention at the following specific conditions:

Evaporator temperature	50°F (10°C)
Condenser temperature	115°F (46.1°C)
Amount of superheat	20°F (11.1 K)
Amount of subcooling	15°F (8.3 K)
Compressor efficiency	70%

Table 1

Composition (wt%)	GWP (AR4)	Average Temp Glide, °C	Relative Capacity to R-32 (%)	Relative COP to R-32 (%)	Compr Disch Temp, °C
R-32 (100)	675	0	100	100	84
Comparative compositions					
R32/R1234yf/CO_2, wt%					
40/51/9	272	8.3	89.8%	95%	74
21.5/75.5/3	148	8.4	65.3%	98%	65
21.5/72.5/6	148	10.5	71.8%	97%	68
21.5/69.5/9	148	12.3	78.3%	97%	71
R32/R1234yf					
44/56	299	3.5	76.1%	100%	80
R32/ R1234yf/ CO_2, wt%					
59/37/4	399.8	3.9	91.8%	99%	87
59/36/5	399.7	4.4	93.8%	98%	88
59/35/6	400	4.8	95.7%	98%	89
59/34/7	400	5.3	97.7%	98%	90
59/33/8	400	5.7	99.6%	97%	90
59/32/9	400	6.1	102%	97%	91
59/31/10	400	6.4	104%	97%	92
59/30/11	400	6.7	106%	97%	93
59/29/12	400	7.0	107%	96%	93
59/28/13	400	7.3	109%	96%	94
58/38/4	393	4.0	91.3%	99%	87
58/37/5	393	4.5	93.3%	98%	88
58/36/6	393	4.9	95.3%	98%	89
58/35/7	393	5.4	97.2%	98%	89
58/34/8	393	5.8	99.2%	97%	90
58/33/9	393	6.2	101%	97%	91
58/32/10	393	6.5	103%	97%	92
58/31/11	393	6.8	105%	97%	92
57/35/8	386	5.9	96.8%	98%	87.1
56/36/8	380	6.0	96.3%	98%	86.8
55/37/8	373	6.1	95.8%	98%	86.4
54/38/8	366	6.2	95.3%	98%	86.1
53/40/7	359	5.9	92.9%	98%	85.3

R32/ R1234yf/ CO_2, wt%					
52/41/7	353	6.1	92.4%	98%	84.9
51/42/7	346	6.2	9.8%	98%	84.6
50/43/7	339	6.3	91.3%	98%	84.3
49/44/7	333	6.5	90.7.%	98%	84.0
48/45/7	326	6.6	90.1%	98%	83.7
47/46/7	319	6.7	91.7%	98%	87
47/45/8	319	7.2	93.7%	97%	87
47/44/9	319	7.6	95.7%	97%	88
47/43/10	319	8.0	97.8%	97%	89
47/42/11	319	8.3	100%	97%	90
47/41/12	319	8.7	102%	96%	90
47/40/13	319	9.0	104%	96%	91
47/39/14	319	9.2	106%	96%	91
47/38/15	319	9.5	108%	95%	92
47/39/16	319	9.7	110%	95%	93
44/49/7	299	7.2	90.1%	98%	86
44/48/8	299	7.7	92.1%	98%	87
44/47/9	299	8.1	94.2%	97%	87
44/46/10	299	8.5	96.2%	97%	88
44/45/11	299	8.8	98.2%	97%	89
44/44/12	299	9.2	100%	96%	89
44/43/13	299	9.5	102%	96%	90
44/42/14	299	9.8	104%	96%	91
44/41/15	299	10.0	106%	95%	91
44/40/16	299	10.3	108%	95%	92
44/39/17	299	10.5	110%	95%	93
43/48/9	292	8.0	90.7%	94%	83
43/47/10	292	8.4	92.5%	94%	84
43/46/11	292	8.7	94.3%	93%	84
43/45/12	292	9.0	96.1%	93%	85
43/44/13	292	9.3	97.9%	93%	86
43/43/14	292	9.6	100%	92%	86
43/42/15	292	9.8	101%	92%	87
43/41/16	292	10.1	103%	91%	87

R32/ R1234yf/ CO_2, wt%					
43/40/17	292	10.3	105%	91%	87
42/49/9	286	8.2	90.1%	94%	83
42/48/10	286	8.5	91.8%	94%	84
42/47/11	285	8.9	93.6%	93%	84
42/46/12	285	9.2	95.4%	93%	85
42/45/13	285	9.5	97.2%	92%	85
42/44/14	285	9.8	99.0%	92%	86
42/43/15	285	10.0	101%	92%	86
42/42/16	285	10.2	103%	91%	87
42/41/17	285	10.4	104%	91%	87

[0119] All the compositions of the present invention provided in Table 1 provide volumetric capacity within ±10% of that for R-32, while providing average temperature glide less than 8°C and having reasonable compressor discharge temperatures as compared to R-32. Many of the compositions of Table 1 provide volumetric capacity within ±5% of that for R-32. Additionally, some of the compositions of Table 1 provide volumetric capacity within ±2% of that for R-32. And all of the compositions show reasonable energy efficiency (as COP relative to R-32).

REFERENCES CITED IN THE DESCRIPTION

Cited references

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Patent documents cited in the description

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- US20070284555A [0091]

Non-patent literature cited in the description

- CHEMICAL ABSTRACTS, 6629-10-3 [0082]
- CHEMICAL ABSTRACTS, 32687-78-8 [0082]
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- CHEMICAL ABSTRACTS, 94-91-7 [0082]
- CHEMICAL ABSTRACTS, 60-00-4 [0082]

SAMMENSÆTNINGER INDEHOLDENDE DIFLUORMETHAN, TETRAFLUORPROPEN OG CARBONDIOXID OG ANVENDELSER DERAF

PATENTKRAV

1. Sammensætning omfattende en kølemiddelblanding til erstatning af R-32-kølemiddelblandingen, der navnlig består af fra ca. 42 til ca. 59 vægtprocent difluormethan, ca. 28 til ca. 53 vægtprocent 2,3,3,3-tetrafluorpropen og ca. 4 til ca. 17 vægtprocent carbondioxid.

2. Sammensætning ifølge krav 1, idet kølemiddelblandingen navnlig består af fra ca. 42 til ca. 59 vægtprocent difluormethan, ca. 33 til ca. 48 vægtprocent 2,3,3,3-tetrafluorpropen og ca. 6 til ca. 15 vægtprocent carbondioxid.

3. Sammensætning ifølge krav 1, idet kølemiddelblandingen navnlig består af ca. 47 til 59 vægtprocent difluormethan, ca. 32 til 47 vægtprocent 2,3,3,3-tetrafluorpropen og ca. 8 til 13 vægtprocent carbondioxid.

4. Sammensætning ifølge krav 1, idet kølemiddelblandingen navnlig består af ca. 47 til 59 vægtprocent difluormethan, ca. 28 til 46 vægtprocent 2,3,3,3-tetrafluorpropen og ca. 4 til 16 vægtprocent carbondioxid.

5. Sammensætning ifølge krav 1, idet kølemiddelblandingen navnlig består af ca. 47 til 59 vægtprocent difluormethan, ca. 31 til 44 vægtprocent 2,3,3,3-tetrafluorpropen og ca. 6 til 13 vægtprocent carbondioxid.

6. Sammensætning ifølge krav 1, idet kølemiddelblandingen navnlig består af ca. 42 til 44 vægtprocent difluormethan, ca. 48 til 49 vægtprocent 2,3,3,3-tetrafluorpropen og ca. 7 til 10 vægtprocent carbondioxid.

7. Sammensætning ifølge krav 1, idet kølemiddelblandingen navnlig består af ca. 43 til 44 vægtprocent difluormethan, ca. 48 til 49 vægtprocent 2,3,3,3-tetrafluorpropen og ca. 6 til 8 vægtprocent carbondioxid.

8. Sammensætning ifølge krav 1, idet kølemiddelblandingen navnlig består af ca. 55 til 59 vægtprocent difluormethan, ca. 33 til 35 vægtprocent 2,3,3,3-tetrafluorpropen og ca. 7 til 12 vægtprocent carbondioxid.

9. Sammensætning ifølge krav 1, idet kølemiddelblandingen navnlig består af ca. 57 to 59 vægtprocent difluormethan, ca. 33 til 34 vægtprocent 2,3,3,3-tetrafluorpropen og ca. 7 til 9 vægtprocent carbondioxid.

10. Sammensætning ifølge krav 1, der endvidere omfatter én eller flere bestanddele valgt fra gruppen bestående af smøremidler, farvestoffer, opløsningsmidler, kompatibiliseringsmidler, stabiliseringsmidler, sporstoffer, midler mod slitage, ekstremtrykmidler, korrosions- og oxideringshæmmere, metaloverfladeenergireduktionsmidler, metaloverfladedeaktivatorer, frie radikalfangere, skumstyringsmidler, viskositetsindeksforbedrende midler, flydepunktnedsættende additiver, detergenter, viskositetsjusteringsmidler og blandinger deraf.

11. Sammensætning ifølge krav 10, hvor smøremidlet er valgt fra gruppen bestående af mineralolie, alkylbenzen, polyolestere, polyalkylenglycoler, polyvinylethere, polycarbonater, perfluorpolyethere, syntetiske paraffiner, syntetiske naphthener, polyalphaolefiner og kombinationer deraf.

12. Fremgangsmåde til frembringelse af kulde omfattende kondensering af sammensætningen ifølge krav 1 og derefter fordampning af sammensætningen i nærheden af et legeme, der skal afkøles.

13. Fremgangsmåde til frembringelse af varme omfattende fordampning af sammensætningen ifølge krav 1 og derefter kondensering af sammensætningen i nærheden af et legeme, der skal opvarmes.

14. Fremgangsmåde til erstatning af R-32 i køle-, luftkonditionerings- eller varmepumpesystemer omfattende tilvejebringelse af sammensætningen ifølge krav 1 som erstatning for R-32.

15. Luftkonditionerings- eller varmepumpesystem, der omfatter en fordamper, kompressor, kondensator og ekspansionsanordning, der er kendetegnet ved at indeholde sammensætningen ifølge krav 1.