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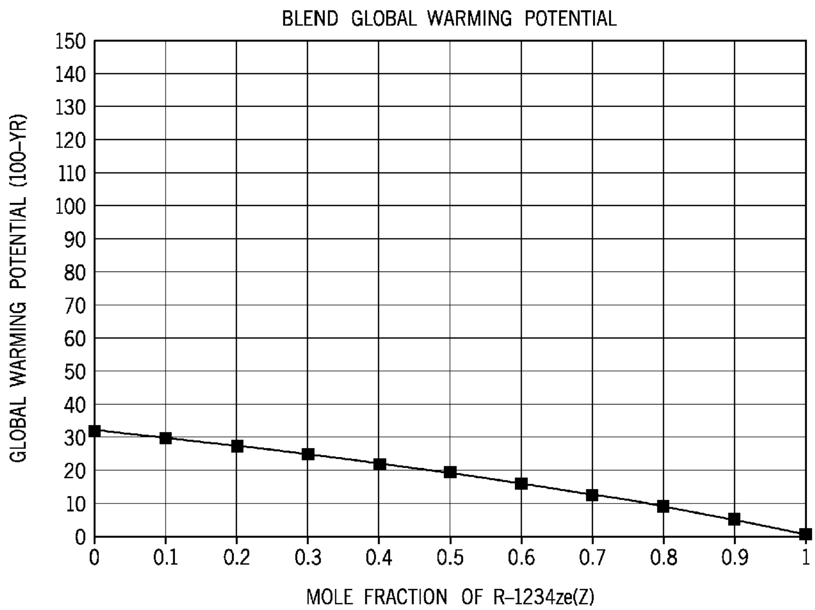

FIG. 4

(57) Abstract: A chemical blend includes 1,1,1,4,4,4-hexafluorobutene and at least one balancing solvent. The balancing solvent is at least one hydrofluoro-olefin, ethylene chloride, methylene chloride, ammonia, at least one ester, at least one hydrocarbon, at least one fluoroether, or a combination thereof. The chemical blend is a substantially-azeotropic blend with a low global warming potential. A method retrofits equipment designed to run with a predetermined refrigerant having a refrigerant molecular weight. The method includes combining cis-1,1,1,4,4,4-hexafluoro-2-butene with at least one balancing solvent to form a replacement refrigerant blend having a blend average molecular weight within 3% of the refrigerant molecular weight. The method also includes placing the replacement refrigerant blend in the equipment in place of the predetermined refrigerant.

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REFRIGERANT COMPOSITIONS AND LOW GLOBAL-WARMING-POTENTIAL BLENDS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to and the benefit of U.S. Provisional Application No. 62/325,786 filed on April 21, 2016, entitled "REFRIGERANT COMPOSITIONS AND LOW GLOBAL-WARMING-POTENTIAL BLENDS," which is hereby incorporated by reference in its entirety for all purposes.

BACKGROUND

[0002] The present disclosure is generally directed to chemical blends with low global warming potential and to refrigerant compositions, and specifically to refrigerant compositions for use in chillers and to substantially-azeotropic fluorinated refrigerant mixtures.

[0003] This section is intended to introduce the reader to various aspects of art that may be related to various aspects of the present disclosure, which are described below. This discussion is believed to be helpful in providing the reader with background information to facilitate a better understanding of the various aspects of the present disclosure. Accordingly, it should be understood that these statements are to be read in this light, and not as admissions of prior art.

[0004] Historically, refrigerants used for heating, ventilating, and air conditioning (HVAC) applications have included chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), and fluorocarbons (FCs). Many of these gases have been associated with global warming. These gases have been assigned a global warming potential (GWP) that provides an indication of their possible contribution to global warming – the higher the GWP of a gas, the greater its expected contribution to global warming. Many of the common refrigerants used in HVAC applications have high GWPs, and there is an industry-wide effort to identify environmentally friendlier replacements for these refrigerants.

[0005] In some countries, the use of high-GWP gases, such as fluorinated gases, has been further discouraged by a tax implemented on their usage, referred to as an f-tax. For example, in Europe an f-tax is to be fully implemented in 2016, based on the GWP of the gas. The GWP of a gas is expressed as a factor relative to carbon dioxide, whose GWP is standardized to a value of one. GWP is based on a number of factors. Currently, these factors include the radiative efficiency of each gas relative to that of carbon dioxide and the decay rate of each gas relative to that of carbon dioxide, as well as other possible factors. The Intergovernmental Panel on Climate Change (IPCC) is responsible for generating the generally-accepted values for GWP, which may be updated from time to time. Currently a GWP value of 150 or less is desirable, since this value is the upper limit for use in mobile air conditioning (such as automotive air conditioning), home refrigerators, and chillers (both centrifugal and positive displacement chillers) in accordance with the current European f-gas laws. This value is also the upper limit for f-gas taxes established by those laws in some European countries and may be used as an upper GWP limit for other applications in future regulations. Of course, the GWP value for gases that triggers the f-tax is subject to change, so lower values are desirable.

[0006] A goal is to replace current refrigerants, which have a high GWP, with effective refrigerants having lower, acceptable GWPs. Of course, an acceptable GWP is but one factor in determining whether a refrigerant is effective. However, it is desirable to replace existing refrigerants with more environmentally-acceptable refrigerants that may be utilized in currently existing HVAC systems. The effective refrigerants desirably have a GWP of no greater than 150.

[0007] Low-pressure chillers normally use non-code vessels, since the working pressures are normally below 15 psig (0.103 MPa), which exempts them from American Society of Mechanical Engineers (ASME) requirements. In the early 1900s, methylene chloride and dichloroethylene were primarily used for low-pressure centrifugal chillers. After its introduction in the 1930s and until the 1990s, CFC-11 (CCl_3F) was the dominant refrigerant for low-pressure centrifugals. Subsequently, CFC-11 has been substantially replaced in centrifugal chillers, with HCFC-123 ($CHCl_2CF_3$) being commonly used as a low pressure refrigerant and hydrofluorocarbon (HFC)-134a (CH_2FCF_3) being commonly used as a higher pressure refrigerant.

[0008] As refrigerant technology continues to advance, alternatives to HCFC-123 have begun to emerge. One alternative is R-1233zd(E) (trans-$CF_3CH{=}CHCl$), although R-1233zd(E) has a significantly higher vapor pressure that requires the use of an ASME pressure vessel and is not suitable for retrofit. Another alternative is R-1336mzz(Z) (cis-$CF_3CH{=}CHCF_3$ or cis-1,1,1,4,4,4-hexafluoro-2-butene, also known as HFO-1336mzz(Z)). However, R-1336mzz(Z) has a significant capacity and efficiency penalty compared to HCFC-123. Additionally, R-1336mzz(Z) has a lower vapor pressure and a lower speed of sound, which reduces chiller capacity. The lower speed of sound also changes the Mach number for the same compressor revolutions per minute (rpm), which may cause efficiency penalties in retrofit situations. Furthermore, compression of saturated vapor goes well inside the vapor dome, which may result in reduced efficiency.

[0009] The retrofitting of existing equipment places additional constraints on the refrigerant selection. For example, when retrofitting a refrigerant into existing equipment, oil miscibility is another important issue. Highly fluorinated compounds, such as the hydrofluoro-olefin (HFO) R-1336mzz(Z), generally have very limited miscibility with the mineral oil used with HCFC-123, which creates difficulties for retrofitting into existing equipment.

SUMMARY

[0010] A summary of certain embodiments disclosed herein is set forth below. It should be understood that these aspects are presented merely to provide the reader with a brief summary of these certain embodiments and that these aspects are not intended to limit the scope of this disclosure. Indeed, this disclosure may encompass a variety of aspects that may not be set forth below.

[0011] It is now recognized that a mixture of R-1234ze(Z) and another HFO is suitable for use as a refrigerant in centrifugal chillers. R-1234ze(Z) is cis-$CF_3CH{=}CHF$, or cis-1,3,3,3-tetrafluoropropene, also known as HFO-1234ze(Z). The other HFO may be R-1336mzz(E). R-1336mzz(E) is trans-$CF_3CH{=}CHCF_3$, or trans-1,1,1,4,4,4-hexafluoro-2-butene, also known as HFO-1336mzz(E). The mixture of cis-1,3,3,3-tetrafluoropropene and trans-1,1,1,4,4,4-hexafluoro-2-butene is an azeotropic or substantially-azeotropic mixture across substantially the entire composition range and may be used as a refrigerant across this range. A substantially-azeotropic composition with an acceptable GWP that also has little or no flammability consists essentially of 1-67 mole percent cis-1,3,3,3-tetrafluoropropene, the balance being an effective amount of trans-1,1,1,4,4,4-hexafluoro-2-butene.

[0012] In some embodiments, a composition is a refrigerant replacement in equipment designed for a predetermined refrigerant. In some embodiments, the replacement refrigerant is a mixture of R-1336mzz(Z) and hydrofluoroether (HFE)-263fb2. HFE-263fb2 is $CF_3CH_2OCH_3$ or 2,2,2-trifluoro methyl ether. In such embodiments, the refrigerant replacement may functionally replace the predetermined refrigerant as a retrofit in the equipment.

[0013] In another embodiment, a chemical blend includes 1,1,1,4,4,4-hexafluorobutene and at least one balancing solvent. The balancing solvent is at least one hydrofluoro-olefin, ethylene chloride, methylene chloride, ammonia, at least one ester, at least one hydrocarbon, at least one fluoroether, or a combination thereof. The chemical blend is a substantially-azeotropic blend with a low global warming potential.

[0014] In another embodiment, a method retrofits equipment designed to run with a predetermined refrigerant having a refrigerant molecular weight. The method includes combining cis-1,1,1,4,4,4-hexafluoro-2-butene with at least one balancing solvent to form a replacement refrigerant blend having a blend average molecular weight within 3% of the refrigerant molecular weight. The method also includes placing the replacement refrigerant blend in the equipment in place of the predetermined refrigerant.

[0015] In another embodiment, a chemical blend includes cis-1,3,3,3-tetrafluoropropene and a nonflammable hydrofluoro-olefin. The blend is a substantially-azeotropic mixture.

[0016] In yet another embodiment, a method of preparing a nonflammable refrigerant blend includes selecting a flammable refrigerant, selecting a nonflammable hydrofluoro-olefin, and combining the nonflammable hydrofluoro-olefin with the flammable refrigerant to form the nonflammable refrigerant. The nonflammable refrigerant is a substantially-azeotropic mixture.

[0017] In accordance with present embodiments, it is now recognized that the R-1234ze(Z)/R-1336mzz(E) mixture may provide improved cycle efficiencies and heat transfer properties relative to other refrigerant substitutes or refrigerant mixtures.

[0018] Another advantage of the R-1234ze(Z)/R-1336mzz(E) mixture is that it is not only an effective substitute for refrigerants now, but it also may be a future substitute for refrigerants. As noted above, the IPCC is responsible for determining the GWP of gases including refrigerants, which determination may be updated from time to time. The R-1234ze(Z)/R-1336mzz(E) mixture has a

GWP that may be adjusted based on the composition of the mixture. Likewise, flammability test results or changes in flammability requirements may be accommodated with changes in the amount of R-1234ze(Z) in the mixture without a major penalty in performance.

[0019] Overall, the R-1234ze(Z)/R-1336mzz(E) mixture may provide a desirable combination of high compressor capacity, inflammability, and low-GWP, which is expected to make it an effective refrigerant substitute in most centrifugal and positive displacement compressor applications.

BRIEF DESCRIPTION OF THE DRAWINGS

[0020] Various aspects of this disclosure may be better understood upon reading the following detailed description and upon reference to the drawings in which:

[0021] FIG. 1 shows the calculated vapor pressure of cis-1,3,3,3-tetrafluoropropene with trans-1,1,1,4,4,4-hexafluoro-2-butene as a mole fraction of cis-1,3,3,3-tetrafluoropropene versus vapor pressure at three different values of α, the mixing parameter constant;

[0022] FIG. 2 shows the relation for cis-1,3,3,3-tetrafluoropropene between mass (weight) fraction and mole fraction in mixtures with trans-1,1,1,4,4,4-hexafluoro-2-butene;

[0023] FIG. 3 shows the temperature glide of the mixture as a function of cis-1,3,3,3-tetrafluoropropene and trans-1,1,1,4,4,4-hexafluoro-2-butene at three different values of α;

[0024] FIG. 4 shows the GWP of the mixture as a function of the concentration of cis-1,3,3,3-tetrafluoropropene and trans-1,1,1,4,4,4-hexafluoro-2-butene;

[0025] FIG. 5 shows the estimated cooling capacity of a mixture in a centrifugal chiller as a function of the concentration of cis-1,3,3,3-tetrafluoropropene and trans-1,1,1,4,4,4-hexafluoro-2-butene at three different values of α;

[0026] FIG. 6 shows the estimated vapor pressure versus composition for R-1336mzz(Z) with methylene chloride, HFE-263fb2, methyl formate, n-hexane, and cyclopentane;

[0027] FIG. 7 shows the estimated vapor pressure of R-1336mzz(E) with cyclopentane, methylene chloride, and ethyl chloride; and

[0028] FIG. 8 shows the estimated vapor pressure of ammonia and R1336-mzz(E) based on published data for R-1234yf and ammonia mixtures.

DETAILED DESCRIPTION

[0029] One or more specific embodiments will be described below. In an effort to provide a concise description of these embodiments, not all features of an actual implementation are described in the specification. It should be appreciated that in the development of any such actual implementation, as in any engineering or design project, numerous implementation-specific decisions must be made to achieve the developers' specific goals, such as compliance with system-related and business-related constraints, which may vary from one implementation to another. Moreover, it should be appreciated that such a development effort might be complex and time consuming, but would nevertheless be a routine undertaking of design, fabrication, and manufacture for those of ordinary skill having the benefit of this disclosure.

[0030] In accordance with the present disclosure, low-GWP blends provide replacements of existing refrigerants, which may be desirable from the perspective of compliance with certain environmental procedures or other similar concerns in many HVAC applications. The blends may also function in heat pumps, especially high temperature heat pumps. Low-GWP blends may also be cost-effective chemicals for foam blowing applications, providing a desirable combination of low vapor density and low cost per unit of mass. Low-GWP blends may also serve as desirable replacement chemicals for cleaning metal, as an aerosol propellant, or other applications in which HFCs, HCFCs, CFCs, and hydrofluoro-olefins (HFOs) have been used in the past. In order to achieve a goal of a low-GWP blend of 150 or less that is nonflammable, while still being an effective refrigerant for applications that may include mobile air conditioning, refrigerators, residential and commercial air conditioning, and other applications that utilize positive displacement compressors, blends of certain gases, such as refrigerants, may be especially desirable.

[0031] An HFO is a compound with a double bond between two carbon atoms that also contains at least one hydrogen atom, at least one fluorine atom, and may optionally include one or more chlorine atoms and additional carbon atoms beyond the two connected with a double bond. The number of carbon atoms generally ranges between 2 and 5 to get compounds with suitable boiling points, but other numbers of carbon atoms may be used in certain situations. It is believed that the fluorine and optional chlorine act to reduce or eliminate flammability of the compound, while the presence of the double bond gives a shorter atmospheric lifetime and low global warming potentials.

[0032] A low global-warming-potential blend includes a substantially-azeotropic mixture of two hydrofluoro-olefins (HFOs). The first HFO is R-1234ze(Z). The second HFO may be R-1336mzz(E). The mixture of cis-1,3,3,3-tetrafluoropropene and trans-1,1,1,4,4,4-hexafluoro-2-butene is an azeotropic or a substantially-azeotropic mixture consisting essentially of about 1 to 67 mole percent R-1234ze(Z), alternatively 10 to 57 mole percent R-1234ze(Z), alternatively 20 to 47 mole percent R-1234ze(Z), alternatively 30 to 37 mole percent R-1234ze(Z), or any range or sub-range therebetween, the balance being an effective amount of R-1336mzz(E), producing a nonflammable or nearly nonflammable azeotropic or substantially-azeotropic mixture. In some embodiments, the mole percentage ranges are selected to provide a blend having a low temperature glide in combination with no flammability. In some embodiments, the temperature glide is a minimum temperature glide. In other embodiments, the temperature glide is less than a predetermined value. The composition may include other ingredients, which in character and/or amount do not affect the advantageous aspects of the mixture as a refrigerant. The ingredients commonly added to refrigerants, which in character and/or amount should not affect their performance as refrigerants, may include lubricants, stabilizers, surfactants, tracers, fluorescent agents, and solubilizing agents. Such ingredients are well-known to those skilled in the HVAC art.

[0033] The mixture of R-1234ze(Z) and R-1336mzz(E) is substantially azeotropic with a normal boiling point of about 10 °C (50 °F). A substantially-azeotropic mixture of R-1234ze(Z) and R-1336mzz(E) having at least about 50% by weight R-1336mzz(E) has a calculated GWP of 32 or less. This substantially-azeotropic mixture of R-1234ze(Z) with an effective amount of R-1336mzz(E) to make it low in toxicity and nonflammable is expected to be an effective refrigerant. Because R-1234ze(Z) has a lower molecular weight than R-1336mzz(E), the substantially-azeotropic mixture of R-1234ze(Z)/R-1336mzz(E) has a lower average molecular weight compared to R-1336mzz(E) alone, which increases the speed of sound within the R-1234ze(Z)/R-1336mzz(E) mixture. The increased speed of sound is particularly effective in providing increased capacity and rotational speed for a centrifugal compressor running at a constant Mach number.

[0034] It is also now recognized that when providing a refrigerant mixture as a replacement refrigerant, it is important that the replacement refrigerant mixture be as close as possible to an azeotrope so as to avoid problems associated with fractional distillation of the mixtures. The composition of the components of the replacement refrigerant mixture must be approximately the same in the vapor state as in the liquid state so as to avoid problems associated with such fractional distillation. In certain embodiments, it may be desirable for the replacement refrigerant to be completely azeotropic, although a replacement refrigerant that is substantially azeotropic also may be utilized successfully. Substantially azeotropic, as used herein, refers to a mixture having a temperature glide of less than about 0.5 °C at 1 atm. Such a mixture generally exhibits no more than a slight amount of fractional distillation that does not affect the characteristics of the mixture as a refrigerant. The mixture also has a low vapor pressure, making it suitable for operation with very high condensing temperatures, such as those required for high temperature heat pump applications, while remaining within component pressure limits. The mixture has a sufficiently high condensing temperature at its vapor pressure so that it operates efficiently as a refrigerant in these high temperature heat pumps.

[0035] The vapor pressure of a blend of R-1234ze(Z) and a selected HFO, R-1336mzz(E) is provided in FIG. 1 for three different values of α as a function of composition, where α is a mixing parameter constant. The vapor pressure may be calculated assuming a regular solution. A regular solution may alternatively be described by Raoult's law modified with a Margules function with only one parameter, α, where

$$P_1 = x_1 P_1^* f_{1,M} \quad \text{(eq. 1)}$$

$$P_2 = x_2 P_2^* f_{2,M} \quad \text{(eq. 2)}$$

where the Margules function is

$$f_{1,M} = \exp(\alpha x_2^2) \quad \text{(eq. 3)}$$

$$f_{2,M} = \exp(\alpha x_1^2) \quad \text{(eq. 4)}$$

where x_1 = mole fraction of component 1

x_2 = mole fraction of component 2

P_1^* = vapor pressure of component 1

P_2^* = vapor pressure of component 2.

[0036] Values of α between 0 and 0.3 provide a good fit with vapor pressure curves for mixtures, here of 1336mzz isomers with other HFOs and HFCs. A value of 0 corresponds to an ideal solution, which means that vapor pressure versus mole fraction of the components is a straight line function. A value of 0.3 results in a moderate increase in vapor pressure above this straight line. A surprising result of this sensitivity analysis is that the temperature glide and other properties of the mixture do not vary much for a range of likely values for α, so it is not necessary to know the exact value of α to show that the mixtures have desirable properties as refrigerants.

[0037] A true azeotrope develops for cases where there is a maximum vapor pressure. For α of 0.3, the calculated azeotrope is very near 0.35 mole fraction of R-1234ze(Z). The temperature glide is very small up to about 0.5 mole fraction, which is the value shown in the example in Table 1, below. For other values of α, the temperature glides, discussed below, are desirably very small, indicating that the mixture is still effectively functioning substantially as an azeotrope for a wide range of α.

[0038] In some embodiments, a blend includes cis-1,3,3,3-tetrafluoropropene and a nonflammable HFO that produces a substantially-azeotropic mixture. A useful mixture is nonflammable and may include cis-1,3,3,3–tetrafluoropropene and the balance a nonflammable HFO. An example nonflammable HFO is trans-1,1,1,4,4,4-hexafluoro-2-butene. The weight percentage for inflammability is expected to be less than about 50% by weight of cis-1,3,3,3-tetrafluoropropene and the balance trans-1,1,1,4,4,4-hexafluoro-2-butene.

[0039] FIG. 2 is provided for convenience and shows the relation between mass fraction (weight) and mole fraction for cis-1,3,3,3-tetrafluoropropene in a mixture with trans-1,1,1,4,4,4-hexafluoro-2-butene. A blend comprising 50% by weight of cis-1,3,3,3-tetrafluoropropene and the balance trans-1,1,1,4,4,4-hexafluoro-2-butene is expected to have a GWP of about 20 or less. Increasing the weight percentage of the trans-1,1,1,4,4,4-hexafluoro-2-butene is an effective method for decreasing the GWP of the mixture. 1,1,1,4,4,4-hexafluoro-2-butene exists in a cis- form as well as a trans- form, and while either form may be used, the trans- form may be preferred for its higher vapor pressure than the cis- form. In one embodiment, the blend consists essentially of cis-1,3,3,3-tetrafluoropropene and trans-1,1,1,4,4,4,-hexafluoro-2-butene as an azeotropic or near azeotropic mixture consisting essentially of about 1 to 66.1 mole percent cis-1,3,3,3-tetrafluoropropene the balance an effective amount of 1,1,1,4,4,4-hexafluoro-2-butene, producing a nonflammable substantially-azeotropic mixture and having a GWP of about 20 or less. The composition of the substantially-azeotropic blend of cis-1,3,3,3-tetrafluoropropene and trans-1,1,1,4,4,4-hexafluoro-2-butene may include other ingredients, which in character and/or amount do not affect the advantageous aspects of the mixture as a refrigerant. The ingredients commonly added to refrigerants which in character and/or amount do not affect the performance as refrigerants include lubricants, stabilizers, surfactants, tracers, fluorescent agents and solubilizing agents.

[0040] Stabilizer(s), when present, may include nitromethane, ascorbic acid, terephthalic acid, azoles such as tolutriazole or benzotriazole, phenolic compounds such as tocopherol, hydroquinone, t-butyl hydroquinone, 2,6-di-tert-butyl-4-methylphenol, epoxides (optionally fluorinated or perfluorinated alkyl or alkenyl or aromatic) such as n-butyl glycidyl ether, hexanediol diglycidyl ether, allyl glycidyl ether, butylphenyl glycidyl ether, phosphites, phosphonates, thiols and lactones, hydrocarbons such as amylene or cyclohexene, and combinations thereof.

[0041] Lubricants, when present, may include mineral oils, silicone oils, paraffins of natural origin, naphthenes, synthetic paraffins, alkylbenzenes, poly-alpha-olefins, polyalkene glycols, polyol esters and/or polyvinyl ethers, and combinations thereof.

[0042] Tracers, when present, are capable of being detected and may include deuterated or nondeuterated hydrofluorocarbons, deuterated hydrocarbons, perfluorocarbons, fluoroethers, brominated compounds, iodinated compounds, alcohols, aldehydes, ketones, nitrous oxide, and combinations thereof.

[0043] Solubilizing agents, when present, may include hydrocarbons, dimethyl ether, polyoxyalkylene ethers, amides, ketones, nitriles, chlorocarbons, esters, lactones, aryl ethers, fluoroethers and 1,1,1-trifluoroalkanes, and combinations thereof.

[0044] Fluorescent agents, when present, may include naphthalimides, perylenes, coumarins, anthracenes, phenanthracenes, xanthenes, thioxanthenes, naphthoxanthenes, fluoresceins and derivatives, and combinations thereof.

[0045] Cis-1,3,3,3-tetrafluoropropene has normal boiling point of about 9.7 °C (about 49.5 °F). It is a relatively simple compound that is easily made using a variety of techniques developed for production of similar two-carbon HFOs, such as the refrigerants R-152a (CH_3CHF_2) and R-134a. According to The Fifth Assessment Report (AR5) of the Intergovernmental Panel on Climate Change (IPCC), R-1234ze(Z)'s GWP is less than one relative to carbon dioxide for a 100-year horizon, with an estimated atmospheric lifetime of only 10 days. By itself, R-1234ze(Z) is moderately flammable. Toxicity data is not available, but similar compounds generally have low toxicity, which gives it a likely A2L classification according to American Society of Heating, Refrigerating, and Air-Conditioning Engineers (ASHRAE) Standard 34, indicating a lower toxicity and a lower flammability with a maximum burning velocity of ≤ 10 cm/s.

[0046] Trans-1,1,1,4,4,4-hexafluoro-2-butene is a nonflammable HFO with a normal boiling point of about 8 °C (about 46.5 °F). The compound also has a cis-isomer with a slightly different boiling point. The GWP of the trans- isomer is not defined in AR5 but is estimated at about 32 in U.S. Pat. App. Pub. No. U.S. 2012/0159976, hereby incorporated by reference herein. Trans-1,1,1,4,4,4-hexafluoro-2-butene appears to have the highest vapor pressure of any known HFO compound that is likely to meet the ASHRAE A1 classification for low toxicity and no flame propagation. While the trans- isomer of 1,1,1,4,4,4-hexafluoro-2-butene is not known to be currently in commercial production, the cis- isomer is already in production. However, it is presently believed that there are no obvious technical barriers to making the trans-isomer compound commercially, and the high vapor pressure may make it the more preferred form of $CF_3CH=CHCF_3$.

[0047] Referring to FIG. 3, cis-1,3,3,3-tetrafluoropropene and trans-1,1,1,4,4,4-hexafluoro-2-butene, when mixed together, form a substantially-azeotropic mixture with a negligible temperature glide over a very wide range of compositions. Temperature glide is the difference between the dew point and the bubble point of a mixture at a given pressure. Stated differently, the temperature glide corresponds to the temperature change between the start of the boiling process and the end of the boiling process at a constant pressure. The temperature glide is the result of the more volatile component evaporating first, which changes the composition and properties of the remaining liquid. The azeotropic properties of a mixture decrease with increasing temperature glide.

[0048] An azeotropic mixture or substantially-azeotropic mixture of two or more components cannot be separated by fractional distillation, a desirable property for refrigerant mixtures. For a non-azeotropic mixture, the composition of the liquid changes during the evaporation process, as the remaining liquid has an increasing concentration of the higher temperature evaporating components. When a mixture is used, for example as a replacement refrigerant, the replacement refrigerant desirably is substantially azeotropic. This is a particularly important consideration in systems that use shell-side condensers and/or evaporators.

[0049] A substantially-azeotropic mixture, one having a temperature glide of 0.5 °C or less between or among the constituents, normally shows negligible effects of separation during phase changes. In order to achieve this temperature glide, the boiling points of the components of the mixture must not be disparate. Here, cis-1,3,3,3-tetrafluoropropene, having a normal boiling point of about 9.7 °C (about 49.5 °F), and trans-1,1,1,4,4,4-hexafluoro-2-butene (an HFO), having a normal boiling point of about 8 °C (about 46.5 °F), are expected to be acceptable. It will be understood by those skilled in the art that other HFOs may also satisfy the requirements for the present blends; however should the boiling point deviate significantly from that of cis-1,3,3,3-tetrafluoropropene, temperature glide is expected to be adversely affected, as is the value of the blend as a refrigerant.

[0050] A graph representing the temperature glide of the mixture of cis-1,3,3,3-tetrafluoropropene and trans-1,1,1,4,4,4-hexafluoro-2-butene is shown in FIG. 3 at three different values of α. As can be seen, the temperature glide of the mixture is very low at all mole fractions of cis-1,3,3,3-tetrafluoropropene (R-1234ze(Z)), even as α increases from 0 to 0.3. With α=0, the maximum temperature glide is less than 0.1 K. With α=0.15, the temperature glide is less than 0.1 K for mole fractions up to about 64% R-1234ze(Z), with a maximum temperature glide of about 0.14 K at about 80% R-1234ze(Z). With α=0.3, the temperature glide is less than 0.1 K for mole fractions up to about 58% R-1234ze(Z), with a maximum temperature glide of about 0.33 K at about 86% R-1234ze(Z).

[0051] Table 1 provides some calculated physical properties for a 50:50 mol%

substantially-azeotropic mixture of cis-1,3,3,3-tetrafluoropropene and trans-1,1,1,4,4,4-hexafluoro-2-butene.

[0052] The base case represents 100% trans-1,1,1,4,4,4-hexafluoro-2-butene, which has a GWP = 2. As can be seen, the weigh percentages of the components of the mixture may be adjusted while maintaining the GWP at an acceptable level below 150 without adversely affecting the substantially azeotropic characteristics of the mixture, as indicated by the temperature glide. Table 1 also shows the capacity ratio in a cooling system of the several different mixtures both in positive-displacement compressors and in centrifugal compressors. FIG. 4 depicts the GWP of the mixture as the mole fraction of R-1234ze(Z) varies from 0, where GWP = 32, the estimated GWP of trans-1,1,1,4,4,4-hexafluoro-2-butene, to a mole fraction of R-1234ze(Z) of one, where GWP = 1, the approximate GWP of cis-1,3,3,3-tetrafluoropropene.

Table 1 Physical Properties of Refrigerant Mixtures

		R-1234ze(Z) mixtures		
	base case	mixing parameter, alpha		
		0	0.15	0.3
Mole fractions:				
R-1336mzz(E)	1	0.5	0.5	0.5
R-1234ze(Z)	0	0.5	0.5	0.5
pressure psia	14.7	14.1	14.6	15.1
mixture molecular weight	164	139	139	139
Mass fractions:				
R-1336mzz(E)	1	0.590	0.590	0.590
R-1234ze(Z)	0	0.410	0.410	0.410
GWP	32	19	19	19
approximate capacity ratio in positive displacement compressor	1.000	**0.956**	**0.992**	**1.030**
approximate capacity ratio in centrifugal compressor	1.000	**1.038**	**1.078**	**1.119**
Temperature glide (K)	0.000	**0.055**	**0.049**	**0.043**

[0053] As previously noted, the bottom curve in FIG. 1 shows the vapor pressure of the mixture as a function of the concentration of cis-1,3,3,3-tetrafluoropropene and trans-1,1,1,4,4,4-hexafluoro-2-butene when the mixing parameter constant α is 0. As expected, since the vapor pressure of trans-1,1,1,4,4,4-hexafluoro-2-butene is the lower of the two components, as the mole fraction of cis-1,3,3,3-tetrafluoropropene is reduced, the vapor pressure of the substantially-azeotropic mixture also is reduced, and pressure reduction follows a straight line relationship, that is, the pressure change is constant with the change in mole fraction of the components. Referring again to Table 1, the capacity ratio of the substantially-azeotropic mixture for a positive displacement compressor is estimated to be directly proportional to the vapor pressure. In accordance with FIG. 1, as the composition of the components of the mixture changes, the vapor pressure also is expected to change, with greater percentages of cis-1,3,3,3-tetrafluoropropene producing higher vapor pressures and therefore higher capacity ratios, which is unexpected, since R-1234ze(Z) used solely as a refrigerant (i.e. mole fraction of R-1234ze(Z) = 1) has a vapor pressure of about 13.4 psia (0.092 MPa), while R-1336mzz(E) has a vapor pressure of about 14.7 psia (0.101 MPa).

[0054] The addition of R-1234ze(Z) to R-1336mzz(E) has other benefits. A lower average molecular weight reduces vapor and liquid density, which reduces the required mass of refrigerant for a particular piece of equipment. Lower density also reduces refrigerant pressure drop, which improves system efficiency or allows smaller refrigerant piping. In addition, the simple structure of R-1234ze(Z) is expected to give better cycle efficiency and a lower evaporator inlet vapor quality, which may further increase the cooling capacity of the mixture beyond the estimates above.

[0055] FIGS. 3, 4, and 5 show temperature glide, global warming potential

(GWP), and cooling capacity, respectively, of R-1234ze(Z) in a mixture with R-1336mzz(E). As with vapor pressure, temperature glide and cooling capacity depend somewhat on the assumed value for alpha (α), so curves for three values of α are included to show the uncertainty. The GWP of the mixture is simply the sum of the mass fraction of each component times the GWP of each component, so it is independent of the value of α.

[0056] The molecular weight of a refrigerant is an important factor in determining its performance in a centrifugal compressor. The speed of sound for a refrigerant mixture is a function of its molecular weight, the speed of sound in a refrigerant mixture being inversely proportional to the square root of the molecular weight. For a centrifugal compressor, the capacity is expected to be proportional to the speed of sound. This relationship suggests that the lower molecular weight of the substantially-azeotropic mixture of cis-1,3,3,3-tetrafluoropropene and trans-1,1,1,4,4,4-hexafluoro-2-butene provides increased capacity. FIG. 5 depicts the cooling capacity of the substantially-azeotropic mixture as a refrigerant in a centrifugal chiller as a function of the composition of cis-1,3,3,3-tetrafluoropropene and trans-1,1,1,4,4,4-hexafluoro-2-butene.

[0057] Acoustic velocity is the speed of sound in a gas. For a centrifugal compressor, the impeller Mach number is the tip speed of the impeller divided by the acoustic velocity of the speed of sound in the gas within the refrigerant system, where the gas is the refrigerant. A higher speed of sound means that the impeller runs faster at the same Mach number, which gives a proportional increase in available cooling capacity.

[0058] The acoustic velocity (c) may be calculated from the following equation:

$$c = (C_p/C_v * R * T/W)^{1/2} \qquad \text{(eq. 5)}$$

where R is the specific gas constant (J/kg*K)

C_p is the constant pressure specific heat (J/kg*K)

C_v is the constant volume specific heat (J/kg*K)

T is the temperature in K and

W is the molecular weight of the refrigerant vapor.

[0059] Generally, the ratio of C_p to C_v does not vary greatly between refrigerants, so the controlling factor in determining the speed of sound is the molecular weight of the refrigerant. Thus, the lower molecular weight for the mixture of cis-1,3,3,3-tetrafluoropropene and trans-1,1,1,4,4,4-hexafluoro-2-butene yields a higher acoustic velocity and a corresponding cooling capacity increase.

[0060] Because of the substantially azeotropic behavior of the cis-1,3,3,3-tetrafluoropropene and trans-1,1,1,4,4,4-hexafluoro-2-butene mixture as determined by its substantially uniform temperature glide across the entire range of composition, the ratio of cis-1,3,3,3-tetrafluoropropene to trans-1,1,1,4,4,4-hexafluoro-2-butene may be tailored to provide a refrigerant that is nonflammable and has an acceptable GWP. Likewise, flammability test results or changes in flammability requirements may be accommodated with changes in the amount of R-1234ze(Z) in the mixture without a penalty in performance from excessive temperature glide.

[0061] In addition, the ratios may be varied to produce refrigerants that operate efficiently in centrifugal compressors or in positive displacement compressors, the ratios being different due to different operating conditions. Again, it is now recognized that the substantially azeotropic nature of the mixture of cis-1,3,3,3-tetrafluoropropene and trans-1,1,1,4,4,4-hexafluoro-2-butene allows the ratios to be changed to lower GWP values as the IPCC modifies global warming potential standards. Thus, some future tuning for GWP is possible. If revisions to the estimated values for GWP of the components increase the calculated GWP value, the concentration of the R-1234ze(Z) (cis-1,3,3,3-tetrafluoropropene) may be increased within the constraints of acceptable flammability to lower the global warming potential of the mixture.

[0062] Mixtures of R-1234ze(Z) and R-1336mzz(E) may also have desirable non-refrigerant applications. As a two-carbon HFO, R-1234ze(Z) is relatively simple to make and may have significantly lower cost than R-1336mzz(E), which means that mixtures are also expected to be less expensive to produce. As mentioned before, the low molecular weight of R-1234ze(Z) provides a lower density in both liquid and vapor phase, which further reduces cost for many applications that required a given volume of fluid. For foam-blowing applications, the combination of lower vapor density and lower cost per unit mass may give much lower cost, which is a major advantage. Other applications may include, but are not limited to, metal cleaning, secondary refrigerants (brine), and aerosol propellants.

[0063] Other variations may include the combination of R-1234ze(Z) with HFOs other than R-1336mzz(E). Exemplary HFOs other than R-1336mzz(E) that may produce an effective mixture include isomers of R-1233zd, other isomers of R-1234ze, R-1234yf ($CH_2{=}CFCF_3$ or 2,3,3,3-tetrafluoropropene, also known as HFO-1234yf), R-1233xf ($CH_2{=}CClCF_3$ or 2-chloro-3,3,3-trifluoropropene), R-1345zfc ($CH_2{=}CHCF_2CF_3$ or 3,3,4,4,4-pentafluoro-1-butene, also known as HFO-1345zfc), HFO-1447fz ($CH_2{=}CHCF_2CF_2CF_3$ or 3,3,4,4,5,5,5-heptafluoro-1-pentene), HFO-1438mzz(E) (trans-$CF_3CH{=}CHCF_2CF_3$ or trans-1,1,1,4,4,5,5,5-octafluoro-2-pentene), R-1336mzz(Z), and combinations thereof. R-1345zfc has a reported normal boiling point of about 5 °C, so it is expected to form substantially-azeotropic mixtures with R-1234ze(Z) and is thus especially attractive in systems with shell-side evaporation and condensation. Other mixtures are expected to have relatively large temperature glide, making them more suitable for use in refrigeration systems with tube-side evaporation and condensation. In the cases of R-1234ze and R-1234yf, the addition of R-1234ze(Z) is expected to lower the vapor pressure, which may allow operation in high temperature heat pumps or other applications with unusually high condensing temperatures while staying within the pressure limits of compressors and other components. Mixtures of more than two components may also be desirable in some cases.

[0064] In some embodiments, a composition is a refrigerant replacement in equipment designed for a predetermined refrigerant. The refrigerant replacement may be selected to have a GWP lower than the GWP of the predetermined refrigerant. The refrigerant replacement may functionally replace the predetermined refrigerant as a retrofit. It may be desirable for the refrigerant replacement to be able to replace the predetermined refrigerant such that the equipment operates without any modification to its structure other than the replacement of the predetermined refrigerant by the refrigerant replacement.

[0065] In some embodiments, the refrigerant replacement is a mixture of two or more compounds. In some embodiments, the refrigerant replacement includes an HFO and a balancing solvent. In some embodiments, the refrigerant replacement has an average molar molecular weight equal to the average molecular weight of the predetermined refrigerant, alternatively an average molar molecular weight within 1% of the average molecular weight of the predetermined refrigerant, alternatively an average molar molecular weight within 2% of the average molecular weight of the predetermined refrigerant, alternatively an average molar molecular weight within 3% of the average molecular weight of the predetermined refrigerant, alternatively an average molar molecular weight within 5% of the average molecular weight of the predetermined refrigerant, alternatively an average molar molecular weight within 10% of the average molecular weight of the predetermined refrigerant, or any range or sub-range therebetween.

[0066] In accordance with an embodiment, a composition for use as a refrigerant replacement in equipment designed for HCFC-123 is a blend of HFO-1336mzz(Z) as the HFO and HFE-263fb2 as the balancing solvent, the blend having a molar average molecular weight near that of HFC-123, which is 152.93 g/mol. In some embodiments, the molar average molecular weight of the refrigerant replacement is in the range of about 145 to 160 g/mol. In some embodiments, an optimum blend depends on matching the speed of sound to provide an optimum compressor mach number for the head conditions for optimum compressor performance, while at the same time assuring that the blend remains nonflammable. Other lower molecular weight components as balancing solvents may include, but are not limited to, other fluorinated ethers, methylene chloride (R-30), hydrocarbons such as cyclopentane, and ammonia. Ammonia and R-1336mzz(E) mixtures may be especially desirable in positive displacement systems, since the mixtures are expected to be nonflammable, but with capacity and vapor pressure near that of ammonia.

[0067] Table 2 summarizes the estimated performance of blends of R-1336mzz(Z) with certain balancing solvents, with the blends having mixture molecular weights near that of R-123. FIG. 6 shows the expected vapor pressures of blends of R-1336mzz(Z) with methylene chloride, HFE-263fb2, n-hexane, methyl formate, and cyclopentane as a function of mole fraction.

[0068] HFE-263fb2 as a balancing solvent is expected to have much better miscibility, since it contains less fluorine and it includes a methyl ester ($-OCH_3$) group. HFEs with this group have good miscibility with hydrocarbons. For example, $C_3F_7OCH_3$ (HFE-7000) is used as a solvent and is fully miscible with toluene. For HFE-263fb2, the solubility with hydrocarbons is expected to be even better, since it contains less fluorine. This improved solubility may allow the use of hydrocarbon lubricants and/or reduce the need for flushing mineral oil from existing systems. Alkylbenzene lubricants are especially attractive for retrofitting. HFE-263fb2 is expected to have excellent stability in blends with R-1336mzz(Z).

Table 2: Comparison of R-1336mzz(Z) blends

	R-30	R-30 azeo.	n-hexane	cyclo-pentane	HFE-263fb2	methyl formate	R-1336 mzz(Z)

Mole fraction	0.139	0.400	0.141	0.117	0.220	0.106	1.00
Mass fraction	0.077	0.257	0.079	0.054	0.164	0.041	1.00
Molecular weight	153	132	153	153	153	153	164
Temp. Glide (°C)	1.1	0.0	0.1	1.1	0.1	0.0	0.0
Capacity[1]	0.972	0.988	0.806	0.988	0.836	0.813	0.799
Centrifugal Capacity[1]	0.972	1.062	0.806	0.988	0.836	0.813	0.772
Centrifugal Capacity[2]	1.259	1.376	1.044	1.280	1.082	1.053	1.00

[1] R-123=1

[2] R-1336mzz(Z)=1

[0069] In some embodiments, R-1336mzz(Z) blends with HFE-263fb2 provide a replacement refrigerant with a low GWP for low-pressure applications. HFE-263fb2, is a flammable fluorinated ether with a measured normal boiling point of 31.6 °C (88.9 °F) that was considered as a foam blowing agent in the 1990s. AR5 lists its atmospheric life as 23 days with a 100-year GWP of 1. It has not been considered as a refrigerant mainly because of its flammability. It is easily synthesized from trifluoroethanol, which is commercially available from multiple suppliers. HFE-263fb2 may currently be used as a chemical intermediary for making fluorinated anesthetics.

[0070] The azeotrope with methylene chloride as the balancing solvent is expected to have properties close to that for CFC-11, which has an average molecular weight of 137.37 g/mol, and may serve as a retrofit fluid in old chillers, especially those with open-drive motors, where compatibility with motor insulation is not an issue.

[0071] Blends with methylene chloride as the balancing solvent may also include one or more stabilizers. Common stabilizers for methylene chloride include methanol, ethanol, t-butylamine and/or hydrocarbons such as cyclohexane, cyclohexene, or amylene at levels of 0.005 to 0.2%. Higher levels of stabilizers (up to roughly 1 or 2% by weight) may be added to nearly azeotropic mixtures without affecting the flammability classification, which may allow the use of aluminum impellers with the mixture.

[0072] The blend with n-hexane as the balancing solvent is essentially azeotropic but may become flammable at concentrations that match the molecular weight of R-123.

[0073] The blend with cyclopentane as the balancing solvent that matches the molecular weight of R-123 is expected give close to the same capacity in a centrifugal chiller and is an especially desirable replacement. The amount of cyclopentane is likely to be near the amount to produce a flammable mixture, so it may be desirable to reduce the amount of cyclopentane to keep the mixture nonflammable.

[0074] Methyl formate may be a desirable balancing solvent that forms mixtures with very little temperature glide. The low molecular weight of methyl formate means only a small amount in a blend is necessary to match the molecular weight of R-123. The lower heat of combustion for methyl formate combined with the small amount of methyl formate required, means that the blend in Table 2 is expected to be nonflammable.

[0075] FIG. 7 shows the expected vapor pressures of blends of R-1336mzz(E) with ethyl chloride, cyclopentane, and methylene chloride as a function of mole fraction.

[0076] In some embodiments, R-1336mzz(E) blends with ammonia provide a replacement refrigerant with a low GWP for high-pressure applications. FIG. 8 shows the calculated vapor pressure of ammonia and R-1336mzz(E) based on published data for R-1234yf and ammonia mixtures. FIG. 8 shows a very flat vapor pressure curve over a broad range compositions with low temperature glides. For centrifugal chillers, a composition of about 10% ammonia by weight is especially desirable since it has a mixture molecular weight similar to that of halocarbon refrigerants such as R-22 and R-134a, which should limit compressor tip-speed requirements.

[0077] For positive displacement systems, a blend with about 50% ammonia by weight as the balancing solvent is especially desirable since it has somewhat higher capacity and lower refrigerant cost. These mixtures are expected to have much lower discharge temperatures, little or no flammability, and lower toxicity than ammonia alone.

[0078] The specific embodiments described above have been shown by way of example, and it should be understood that these embodiments may be susceptible to various modifications and alternative forms. It should be further understood that the claims are not intended to be limited to the particular forms disclosed, but rather to cover all modifications, equivalents, and alternatives falling within the spirit and scope of this disclosure.

CLAIMS

What is claimed is:

1. A chemical blend comprising 1,1,1,4,4,4-hexafluorobutene and at least one balancing solvent selected from the group consisting of at least one hydrofluoro-olefin, ethylene chloride, methylene chloride, ammonia, at least one ester, at least one hydrocarbon, at least one fluoroether, and combinations thereof, wherein the chemical blend is a substantially-azeotropic blend with a low global warming potential.

2. The chemical blend of claim 1, wherein a vapor of the chemical blend shows no flame propagation in air, thereby according a flammability classification 1 in American Society of Heating, Refrigerating, and Air-Conditioning Engineers Standard 34-2013.

3. The chemical blend of claim 1, wherein the balancing solvent comprises ammonia and a weight fraction of the ammonia is selected such that the chemical blend is a replacement refrigerant for a positive displacement compressor.

4. The chemical blend of claim 1, wherein the balancing solvent comprises ammonia and a weight fraction of the ammonia is selected such that the chemical blend is a replacement refrigerant for a centrifugal compressor.

5. The chemical blend of claim 1, wherein the balancing solvent comprises cis-1,3,3,3-tetrafluoropropene.

6. The chemical blend of claim 1, wherein the 1,1,1,4,4,4-hexafluorobutene is cis-1,1,1,4,4,4-hexafluoro-2-butene and the balancing solvent is selected from the group consisting of methylene chloride, $CF_3CH_2OCH_3$, ammonia, ethyl chloride, and combinations thereof.

7. The chemical blend of claim 6, wherein the balancing solvent comprises $CF_3CH_2OCH_3$ and a weight fraction of the $CF_3CH_2OCH_3$ is selected such that the chemical blend is a substantially azeotropic replacement refrigerant for HCFC-123 in a centrifugal chiller.

8. The chemical blend of claim 1, wherein the balancing solvent is selected such that the chemical blend has a molar average molecular weight within 3% of an average molecular weight of a predetermined refrigerant to serve as a replacement refrigerant blend for the predetermined refrigerant.

9. The chemical blend of claim 8, wherein the balancing solvent comprises 2,2,2-trifluoro methyl ether.

10. The chemical blend of claim 8, wherein the balancing solvent comprises ammonia.

11. The chemical blend of claim 8, wherein the balancing solvent is selected from the group consisting of methylene chloride, n-hexane, cyclopentane, methyl formate, and combinations thereof.

12. The chemical blend of claim 8, wherein the predetermined refrigerant is selected from the group consisting of CCl_3F and $CHCl_2CF_3$.

13. A method of retrofitting equipment designed to run with a predetermined refrigerant having a refrigerant molecular weight, the method comprising:

combining cis-1,1,1,4,4,4-hexafluoro-2-butene with at least one balancing solvent to form a replacement refrigerant blend having a blend average molecular weight within 3% of the refrigerant molecular weight; and

placing the replacement refrigerant blend in the equipment in place of the predetermined refrigerant.

14. The method of claim 13 further comprising operating the equipment with the replacement refrigerant blend in place of the predetermined refrigerant.

15. The method of claim 13, wherein the predetermined refrigerant blend has a lower global warming potential than the predetermined refrigerant.

16. The method of claim 13, wherein the balancing solvent is selected from the group consisting of 2,2,2-trifluoro methyl ether, methylene chloride, n-hexane, cyclopentane, methyl formate, and combinations thereof.

17. A chemical blend comprising cis-1,3,3,3-tetrafluoropropene and a nonflammable hydrofluoro-olefin, the blend being a substantially-azeotropic mixture.

18. The chemical blend of claim 17, wherein the nonflammable hydrofluoro-olefin is trans-1,1,1,4,4,4-hexafluoro-2-butene.

19. The chemical blend of claim 18, wherein the chemical blend consists essentially of the cis-1,3,3,3-tetrafluoropropene and the trans-1,1,1,4,4,4-hexafluoro-2-butene.

20. The chemical blend of claim 19, wherein the cis-1,3,3,3-tetrafluoropropene and the trans-1,1,1,4,4,4-hexafluoro-2-butene are in a mole ratio in the range of 1:99 to 67:33.

21. The chemical blend of claim 17 further comprising an additive selected from the group consisting of at least one lubricant, at least one stabilizer, at least one surfactant, at least one tracer, at least one fluorescent agent, at least one solubilizing agent, and combinations thereof.

22. The chemical blend of claim 17, wherein the nonflammable hydrofluoro-olefin is selected from the group consisting of cis-$CF_3CH=CHCl$, trans-$CF_3CH=CHCl$, cis-$CF_3CH=CHCF_3$, trans-$CF_3CH=CHCF_3$, $CH_2=CFCF_3$, $CH_2=CClCF_3$, $CH_2=CHCF_2CF_3$, $CH_2=CHCF_2CF_2CF_3$, trans-$CF_3CH=CHCF_2CF_3$, and combinations thereof.

23. The chemical blend of claim 17, wherein the chemical blend is nonflammable.

24. A method of preparing a nonflammable refrigerant blend comprising:
selecting a flammable refrigerant;
selecting a nonflammable hydrofluoro-olefin; and
combining the nonflammable hydrofluoro-olefin with the flammable refrigerant to form the nonflammable refrigerant, the nonflammable refrigerant being a substantially-azeotropic mixture.

25. The method of claim 24, wherein the nonflammable hydrofluoro-olefin and the flammable refrigerant have a boiling point difference less than 2 °C.

26. The method of claim 24, wherein the flammable refrigerant comprises cis-1,3,3,3-tetrafluoropropene.

27. The method of claim 24, wherein the nonflammable hydrofluoro-olefin comprises trans-1,1,1,4,4,4-hexafluoro-2-butene.

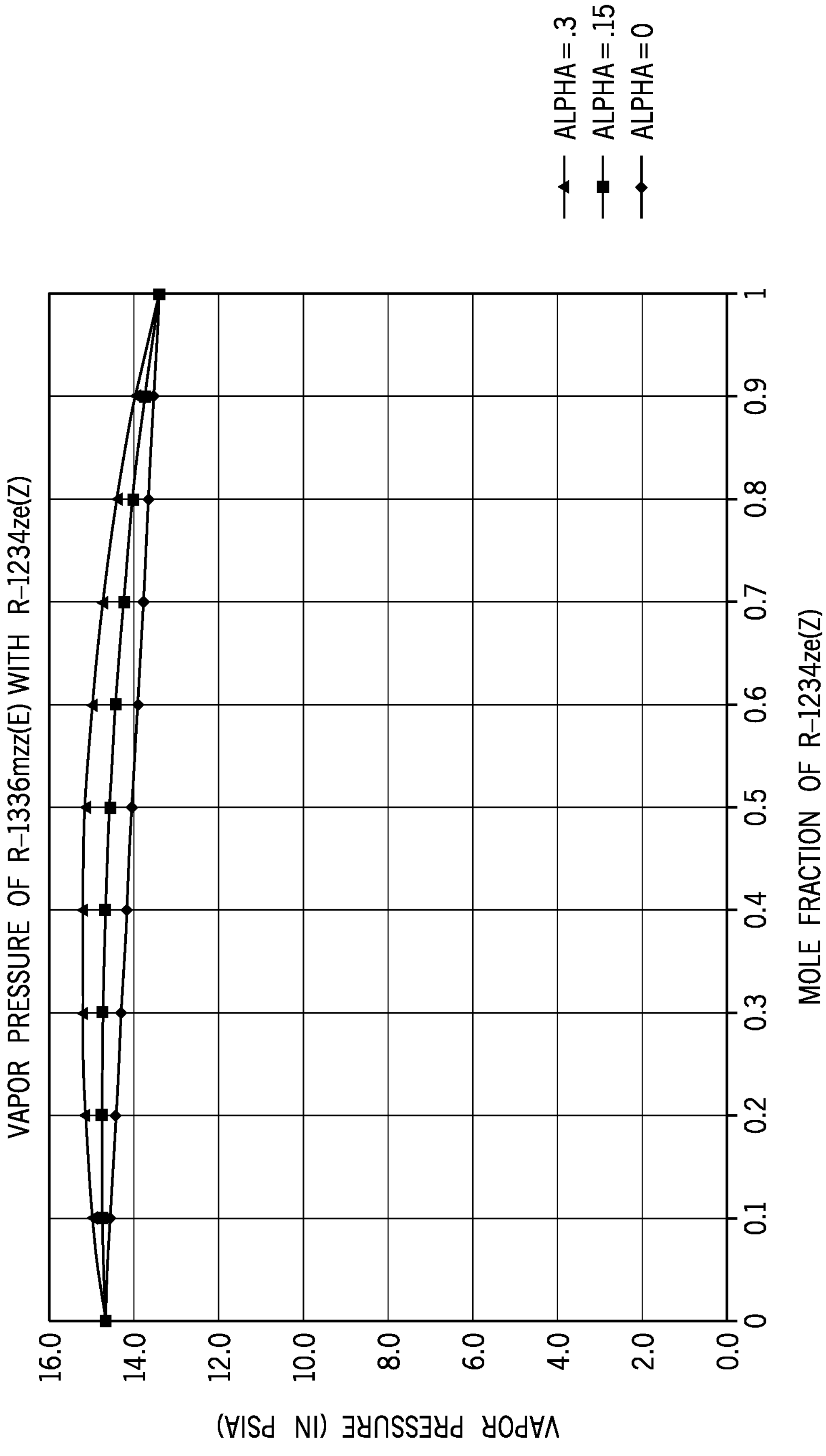
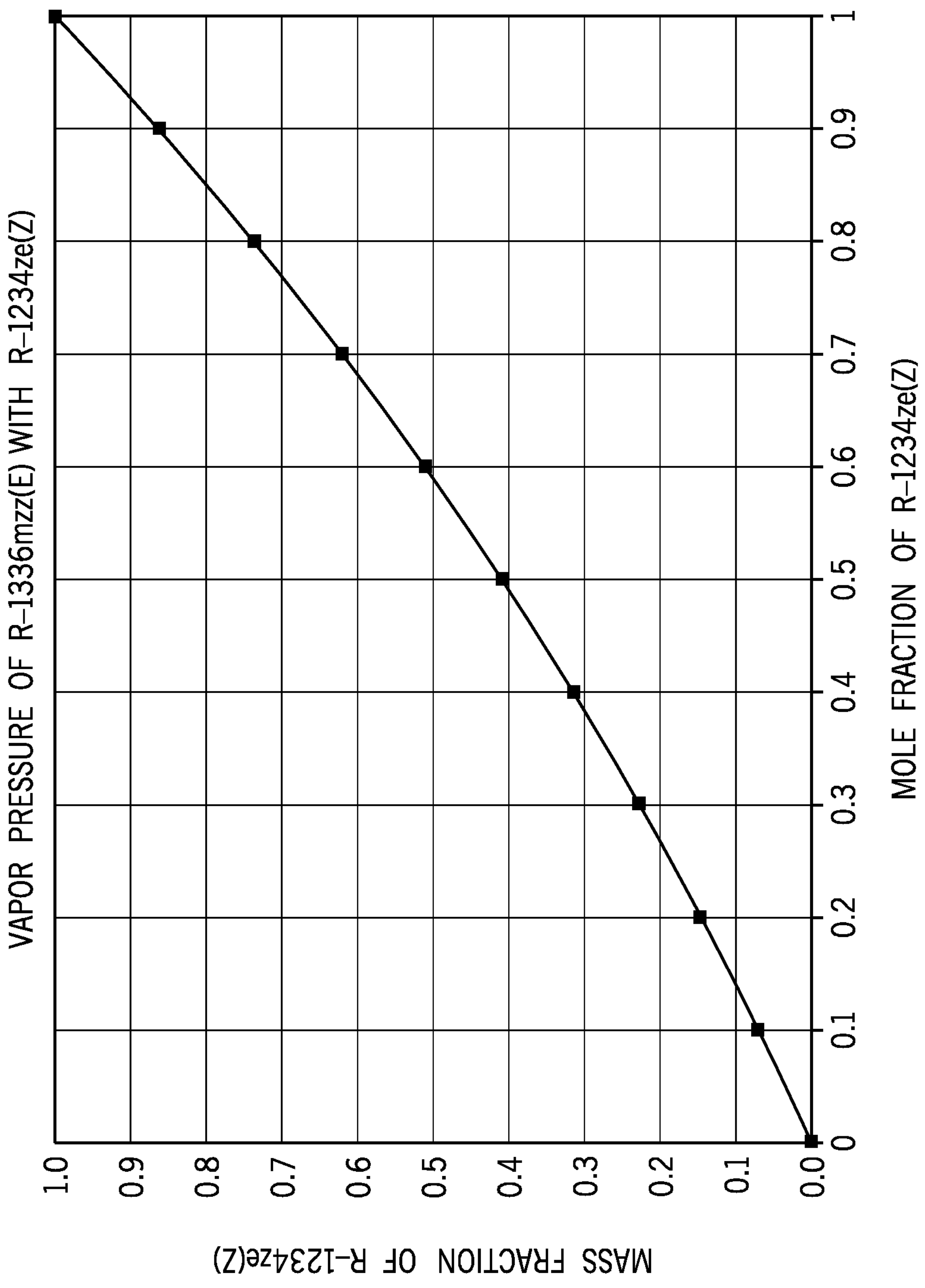

VAPOR PRESSURE OF R-1336mzz(E) WITH R-1234ze(Z)
VAPOR PRESSURE (IN PSIA)
16.0
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
MOLE FRACTION OF R-1234ze(Z)
ALPHA=.3
ALPHA=.15
ALPHA=0

FIG. 1


VAPOR PRESSURE OF R-1336mzz(E) WITH R-1234ze(Z)
MASS FRACTION OF R-1234ze(Z)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
MOLE FRACTION OF R-1234ze(Z)
0
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0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1

FIG. 2

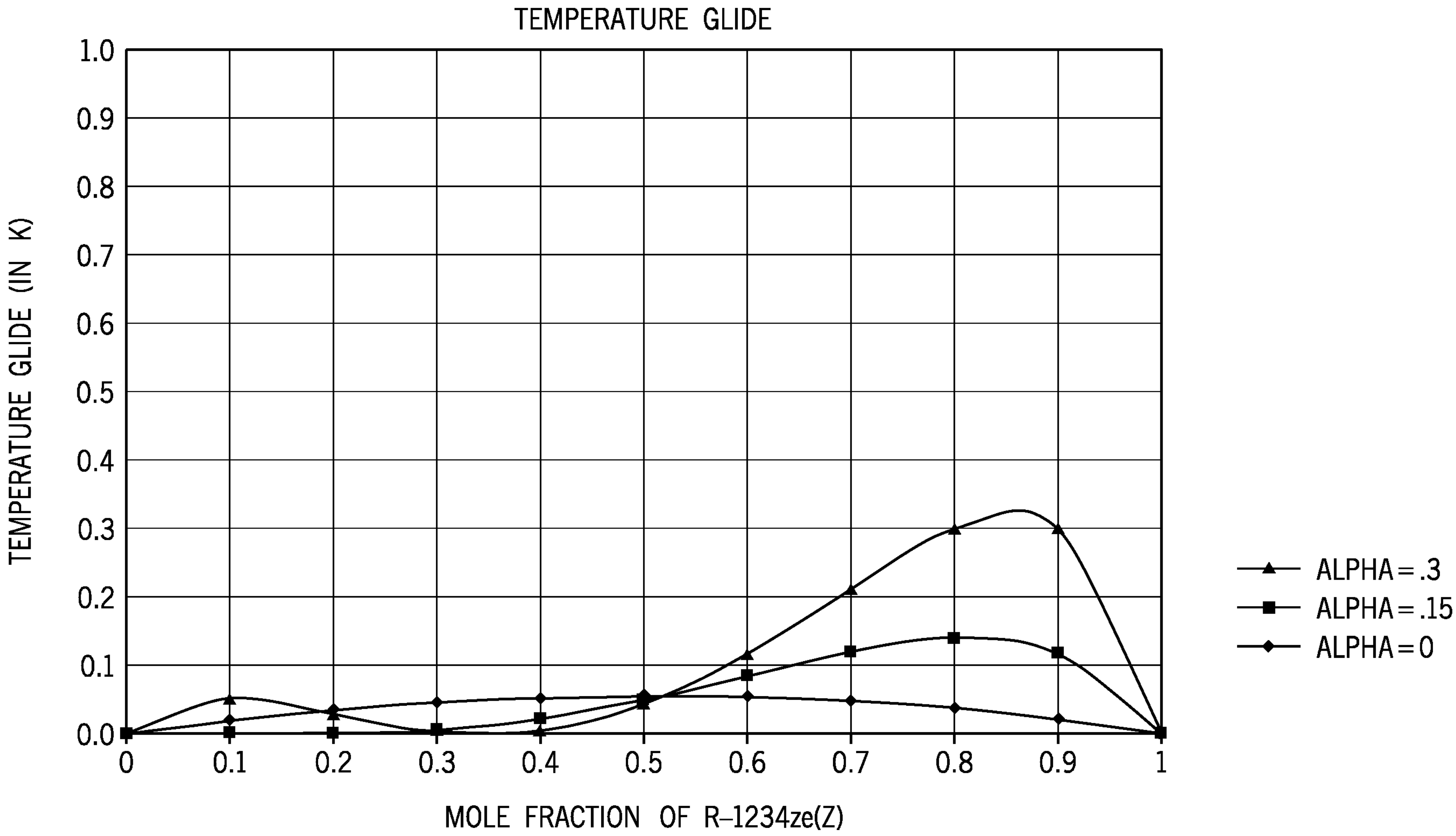
TEMPERATURE GLIDE
TEMPERATURE GLIDE (IN K)
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
MOLE FRACTION OF R–1234ze(Z)
ALPHA=.3
ALPHA=.15
ALPHA=0

FIG. 3

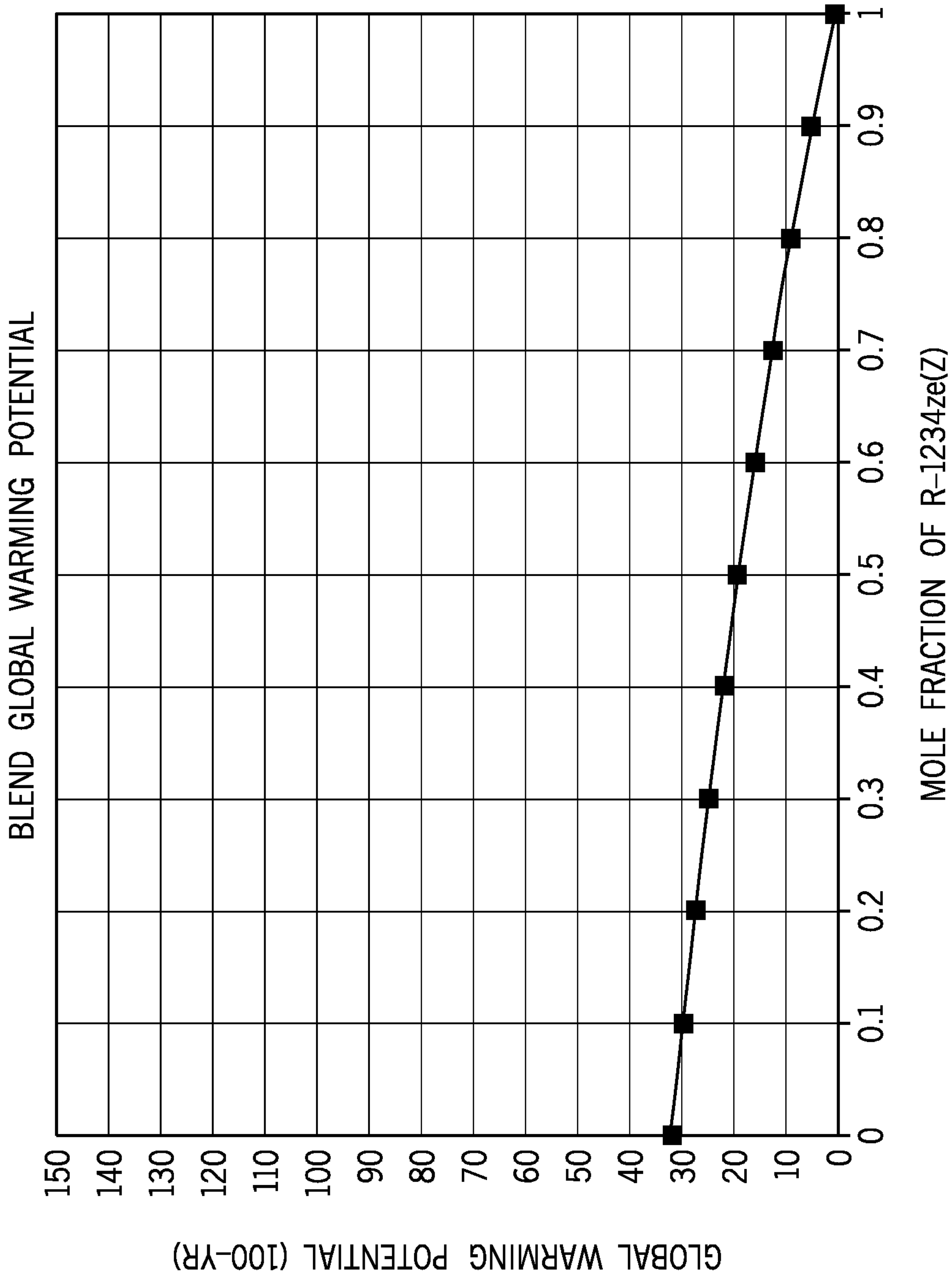
BLEND GLOBAL WARMING POTENTIAL
GLOBAL WARMING POTENTIAL (100-YR)
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
MOLE FRACTION OF R-1234ze(Z)

FIG. 4

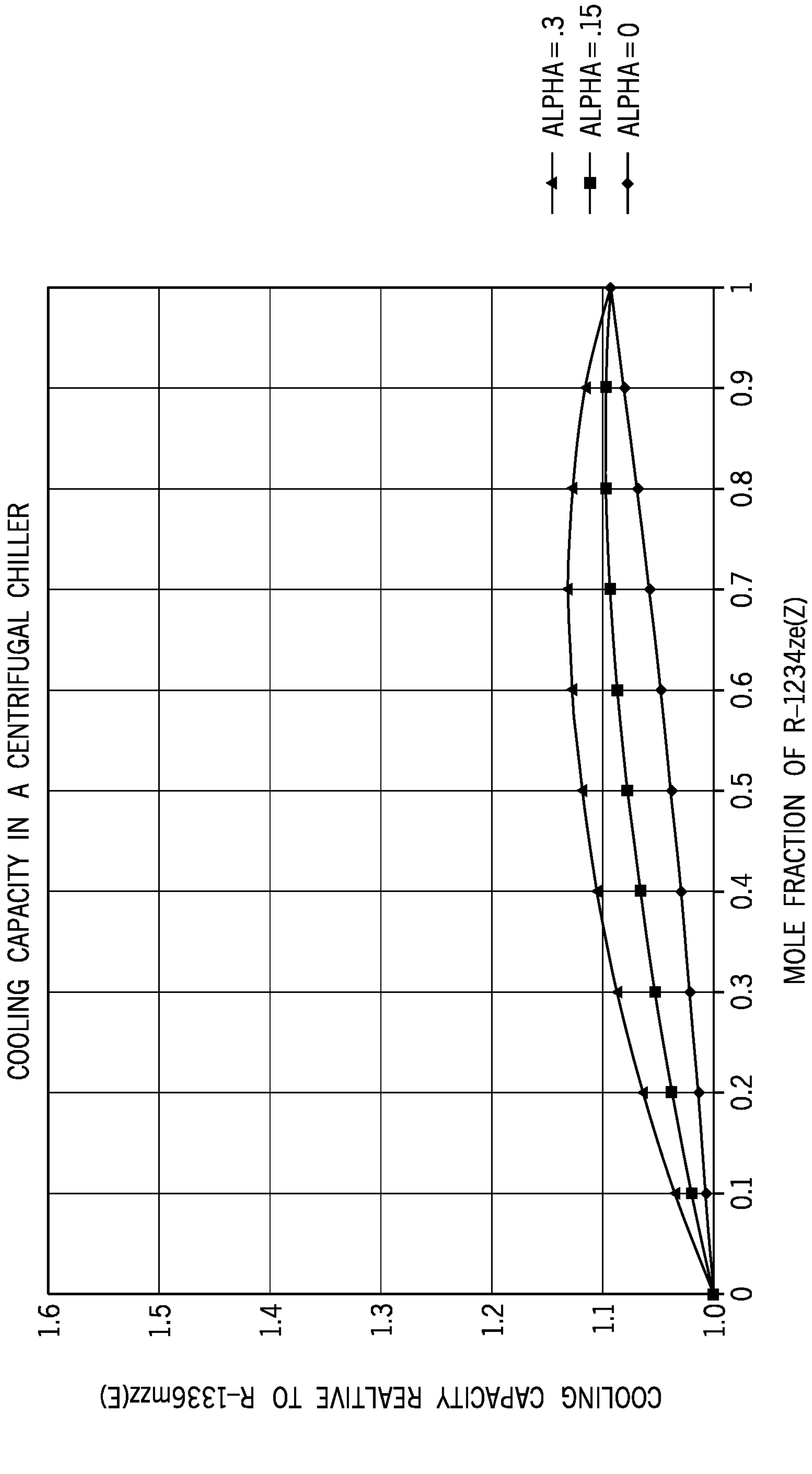
COOLING CAPACITY IN A CENTRIFUGAL CHILLER
COOLING CAPACITY REALTIVE TO R-1336mzz(E)
MOLE FRACTION OF R-1234ze(Z)
1.0
1.1
1.2
1.3
1.4
1.5
1.6
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
ALPHA=.3
ALPHA=.15
ALPHA=0

FIG. 5

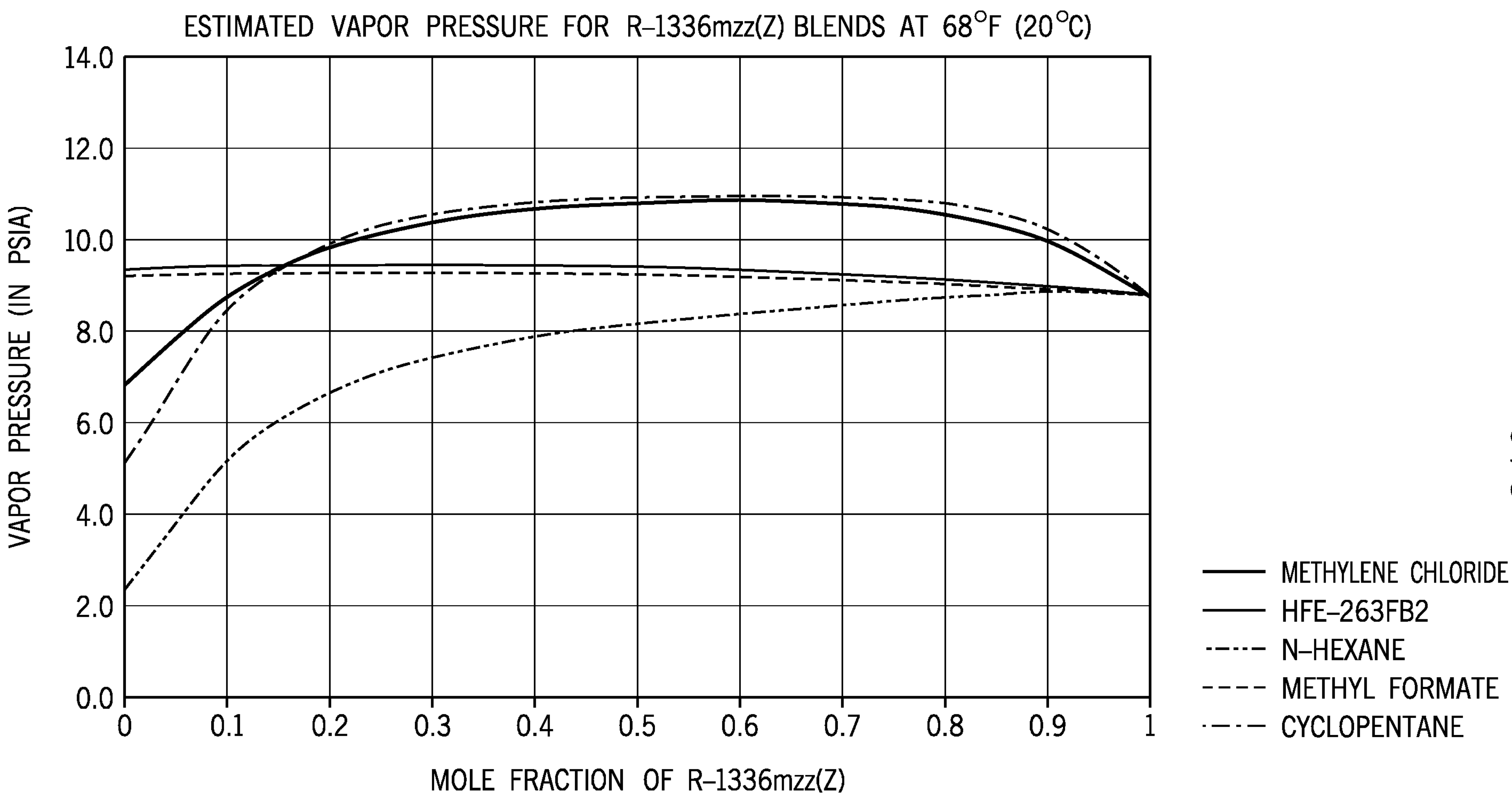
ESTIMATED VAPOR PRESSURE FOR R-1336mzz(Z) BLENDS AT 68°F (20°C)
VAPOR PRESSURE (IN PSIA)
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
MOLE FRACTION OF R-1336mzz(Z)
METHYLENE CHLORIDE
HFE-263FB2
N-HEXANE
METHYL FORMATE
CYCLOPENTANE

FIG. 6

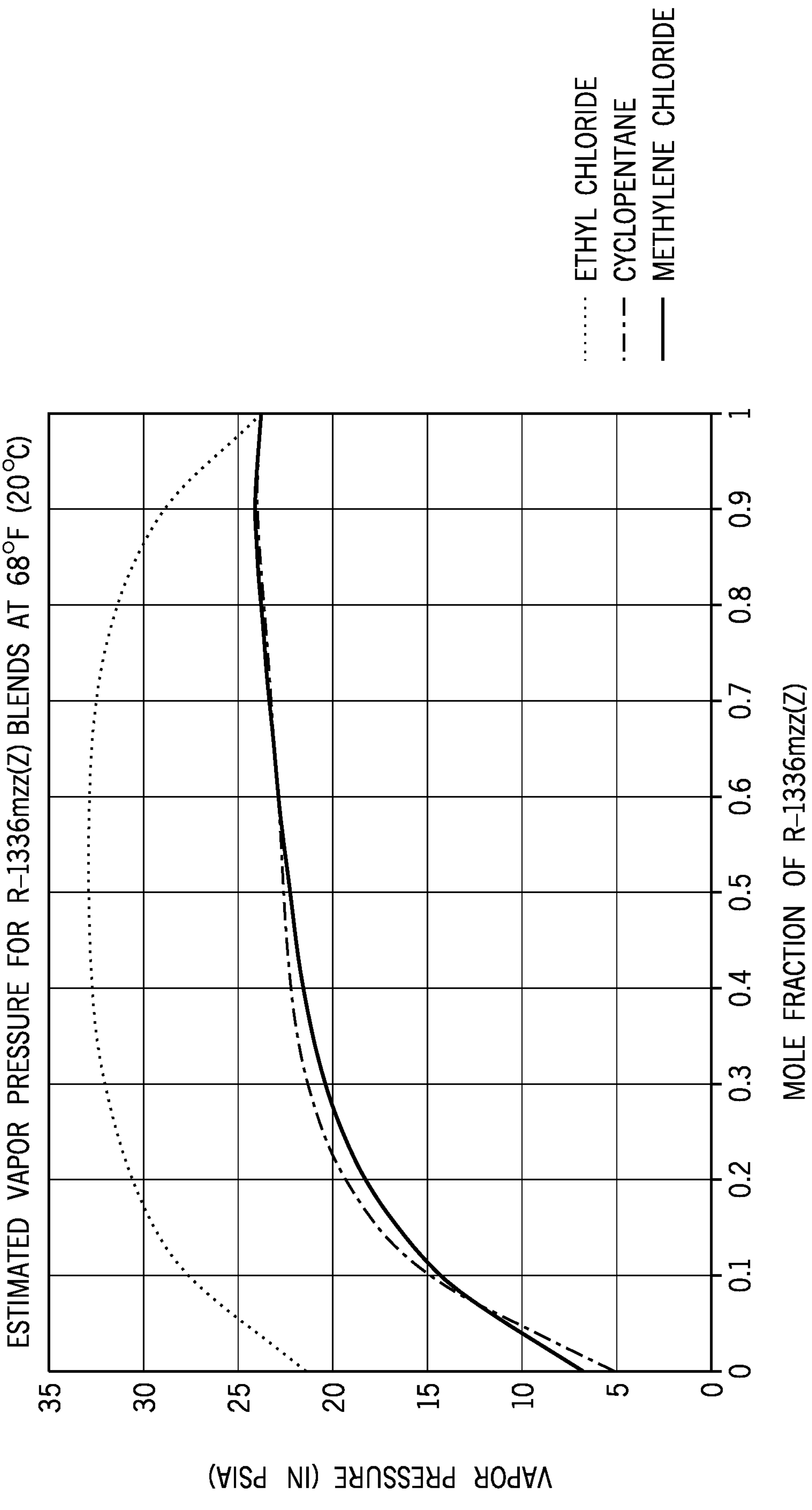
ESTIMATED VAPOR PRESSURE FOR R-1336mzz(Z) BLENDS AT 68°F (20°C)
VAPOR PRESSURE (IN PSIA)
0
5
10
15
20
25
30
35
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
MOLE FRACTION OF R-1336mzz(Z)
ETHYL CHLORIDE
CYCLOPENTANE
METHYLENE CHLORIDE

FIG. 7

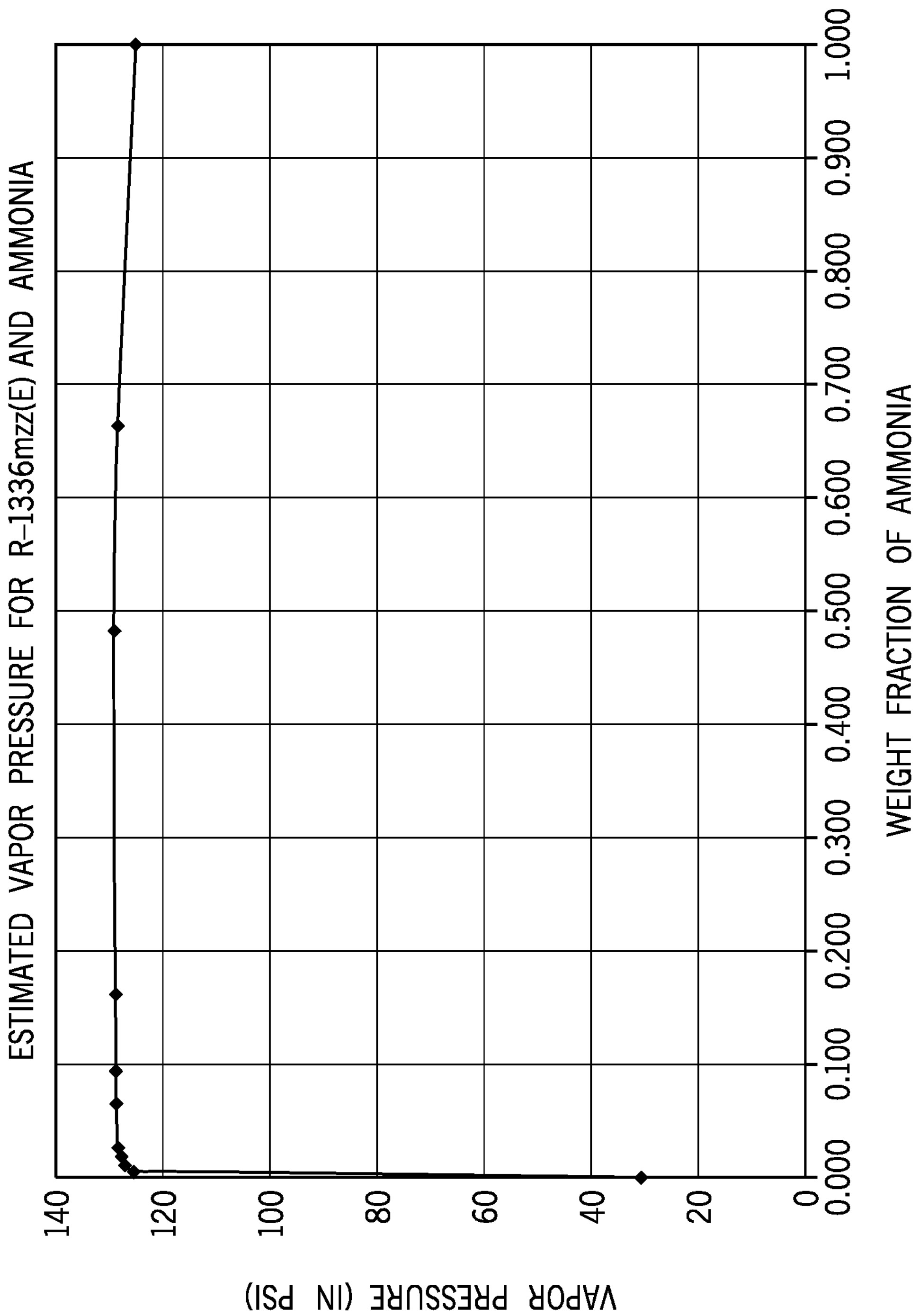
ESTIMATED VAPOR PRESSURE FOR R-1336mzz(E) AND AMMONIA
VAPOR PRESSURE (IN PSI)
0
20
40
60
80
100
120
140
WEIGHT FRACTION OF AMMONIA
0.000
0.100
0.200
0.300
0.400
0.500
0.600
0.700
0.800
0.900
1.000

FIG. 8

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2017/028833

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

5(completely); 1, 2, 8(partially)

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2017/028833

A. CLASSIFICATION OF SUBJECT MATTER
INV. C09K5/04
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2013/255284 A1 (RACHED WISSAM [FR]) 3 October 2013 (2013-10-03) paragraphs [0001], [0077], [0082] - [0084], [0102], [0132], [0134], [0191] -----	1,2,5,8
X	JP 2014 005418 A (CENTRAL GLASS CO LTD) 16 January 2014 (2014-01-16) paragraphs [0018], [0047], [0048], [0079], [0092], [0100], [0109]; claims 18,19 -----	1,2,5,8
X	US 2014/284516 A1 (JOHNSEN MONTFORT A [US]) 25 September 2014 (2014-09-25) paragraphs [0061], [0067], [0082]; figure 4 -----	1,2,5,8
	-/--	

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
20 June 2017	22/08/2017

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Martinez Marcos, V

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Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2017/028833

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2012/004299 A1 (HULSE RYAN [US] ET AL) 5 January 2012 (2012-01-05) paragraphs [0002] - [0005], [0025], [0031], [0044], [0093] - [0096] -----	1,2,8

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2017/028833

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2013255284 A1	03-10-2013	CN 103228758 A	31-07-2013
		CN 105154014 A	16-12-2015
		EP 2643420 A1	02-10-2013
		ES 2511147 T3	22-10-2014
		FR 2968009 A1	01-06-2012
		JP 5905897 B2	20-04-2016
		JP 2014502303 A	30-01-2014
		US 2013255284 A1	03-10-2013
		US 2016115362 A1	28-04-2016
		WO 2012069725 A1	31-05-2012
JP 2014005418 A	16-01-2014	NONE	
US 2014284516 A1	25-09-2014	NONE	
US 2012004299 A1	05-01-2012	AU 2010340049 A1	05-07-2012
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		JP 2016117903 A	30-06-2016
		KR 20120104603 A	21-09-2012
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		RU 2012129847 A	27-01-2014
		US 2012004299 A1	05-01-2012
		US 2015018429 A1	15-01-2015
		US 2017066953 A1	09-03-2017
		WO 2011084447 A2	14-07-2011

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 5(completely); 1, 2, 8(partially)

   a chemical blend comprising 1,1,1,4,4,4-hexafluorobutene and at least one balancing solvent, wherein the chemical blend is a substantially-azeotropic blend with a low global warming potential and the balancing solvent comprises a hydrofluoro-olefin

   ---

2. claims: 12(completely); 1, 2, 6, 8(partially)

   a chemical blend comprising 1,1,1,4,4,4-hexafluorobutene and at least one balancing solvent, wherein the chemical blend is a substantially-azeotropic blend with a low global warming potential and the balancing solvent comprises ethylene chloride or methylene chloride

   ---

3. claims: 3, 4, 10(completely); 1, 2, 6, 8(partially)

   a chemical blend comprising 1,1,1,4,4,4-hexafluorobutene and at least one balancing solvent, wherein the chemical blend is a substantially-azeotropic blend with a low global warming potential and the balancing solvent comprises ammonia

   ---

4. claims: 1, 2, 8(all partially)

   a chemical blend comprising 1,1,1,4,4,4-hexafluorobutene and at least one balancing solvent, wherein the chemical blend is a substantially-azeotropic blend with a low global warming potential and the balancing solvent comprises one ester

   ---

5. claims: 11(completely); 1, 2, 8(partially)

   a chemical blend comprising 1,1,1,4,4,4-hexafluorobutene and at least one balancing solvent, wherein the chemical blend is a substantially-azeotropic blend with a low global warming potential and the balancing solvent comprises one hydrocarbon

   ---

6. claims: 7, 9(completely); 1, 2, 6, 8(partially)

   a chemical blend comprising 1,1,1,4,4,4-hexafluorobutene and at least one balancing solvent, wherein the chemical blend is a substantially-azeotropic blend with a low global warming potential and the balancing solvent comprises one fluoroether

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

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7. claims: 13-16

A method of retrofitting equipment designed to run with a predetermined refrigerant having a refrigerant molecular weight, the method comprising:combining cis-1,1,1,4,4,4-hexafluoro-2-butene with at least one balancing solvent to form a replacement refrigerant blend having a blend average molecular weight within 3% of the refrigerant molecular weight; andplacing the replacement refrigerant blend in the equipment in place of the predetermined refrigerant.

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8. claims: 17-23

A chemical blend comprising cis-1,3,3,3-tetrafluoropropene and a nonflammable hydrofluoro-olefin, the blend being a substantially-azeotropic mixture.

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9. claims: 24-27

A method of preparing a nonflammable refrigerant blend comprising:selecting a flammable refrigerant;selecting a nonflammable hydrofluoro-olefin; andcombining the nonflammable hydrofluoro-olefin with the flammable refrigerant to form the nonflammable refrigerant, the nonflammable refrigerant being a substantially-azeotropic mixture.
