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(71) Applicant *(for all designated States except US)*: **DAIKIN INDUSTRIES, LTD.** [JP/JP]; Umeda Center Building, 4-12, Nakazaki-Nishi 2-Chome, Kita-ku, Osaka-shi, Osaka, 5308323 (JP).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **SHIBANUMA, Takashi** [JP/JP]; c/o Yodogawa Seisakusho, DAIKIN INDUSTRIES, LTD.,1-1, Nishihitotsuya, Settsu-shi, Osaka, 5660044 (JP). **TSUCHIYA, Tatsumi** [JP/JP]; c/o Yodogawa Seisakusho, DAIKIN INDUSTRIES, LTD.,1-1, Nishihitotsuya, Settsu-shi, Osaka, 5660044 (JP). **YAMADA, Yasufu** [JP/JP]; c/o Yodogawa Seisakusho, DAIKIN INDUSTRIES, LTD.,1-1, Nishihitotsuya, Settsu-shi, Osaka, 5660044 (JP).

(74) Agent: **Saegusa & Partners**; Kitahama TNK Building, 1-7-1, Doshomachi, Chuo-ku, Osaka-shi, Osaka, 5410045 (JP).

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**(54) Title:** HFC-1225YE-CONTAINING REFRIGERANT AND REFRIGERANT COMPOSITION CONTAINING THE REFRIGERANT

**(57) Abstract:** An object of the present invention is to provide: a refrigerant that has little effect on the ozone layer and on global warming (low GWP), is nonflammable, and has refrigerant characteristics substantially equivalent to those of known HFC-134a (for car air conditioners) or R410A (for air conditioners); and a method of operating a refrigerator using the refrigerant. The invention provides a refrigerant containing HFC-1225ye containing 90 mol% of (Z)HFC-1225ye, and a method of operating a refrigerator using the refrigerant.

# DESCRIPTION

# HFC-1225ye-CONTAINING REFRIGERANT AND REFRIGERANT COMPOSITION CONTAINING THE REFRIGERANT

## TECHNICAL FIELD

The present invention relates to a refrigerant containing pentafluoropropene (HFC-1225ye; $CHF=CF-CF_3$), a refrigerant composition containing the refrigerant, and a method of operating a refrigerator using the refrigerant. More specifically, the present invention relates to a nonflammable refrigerant containing pentafluoropropene, and particularly a refrigerant containing 90 mol% or more of one specific type of geometric isomer thereof ((Z)HFC-1225ye), and a method of operating a refrigerator using the refrigerant.

## BACKGROUND ART

As refrigerants for refrigerators and heating media for heat pumps (e.g., coolants), chlorofluorocarbon (CFC) and hydrochlorofluorocarbon (HCFC) are mainly used singly. Such refrigerants are collectively referred to as CFCs.

However, it has been noted since the 1980s that CFCs emitted into the atmosphere deplete the ozone layer and cause serious adverse effects on the earth's ecosystem including humans. International agreements have been made regarding the restriction of CFCs having a high risk of ozone layer depletion. Use and production of some CFCs have already been forbidden in advanced countries.

Fluorocarbons called hydrofluorocarbons (HFCs) are mainly used as replacements for chlorofluorocarbons. For example, dichlorodifluoromethane (R12), mainly used as a refrigerant for domestic refrigerators, car air conditioners, turbo refrigerators and container freezers, has been replaced by 1,1,1,2-tetrafluoroethane (HFC-134a), in compliance with the above regulations. Difluorochloromethane (R22) has been replaced by R410A, which is an HFC mixed refrigerant. However, the HFC used as a replacement has a high global warming potential (GWP); use of HFC is allowed only so long as the HFC is not emitted outside.

In such a circumstance, two regulations (F-gas regulations), "Regulation on Certain Fluorinated Greenhouse Gases" and "Directive Relating to Emissions of F-Gas from Air Conditioning Systems Fitted to Cars" were declared by the EU in June, 2006. According to these regulations, mobile air conditioners (car air conditioners) installed in new vehicle models sold on the market from 2011, and those in all vehicles sold from 2017 must be configured to use a refrigerant having a GWP of not more than 150.

HFC-134a in current use has a GWP of 1,300. Therefore, HFC-134a is a refrigerant restricted by these regulations. As a replacement for HFC-134a, the use of carbon dioxide ($CO_2$) with an extremely low GWP of 1 has been studied; however, it has defects such as high pressure, an increase in refrigerator volume, and low refrigeration efficiency.

The use of HFC refrigerants having a low global warming potential has also been proposed. For example, Patent Document 1 (Japanese Unexamined Patent Publication No. 1992-110388) discloses using an HFC propene compound as a refrigerant. Specific examples thereof include fluoropropene (HFC-1261yf; $CH_3CF=CH_2$), trifluoropropene (HFC-1243zf; $CF_3CH=CH_3$, HFC-1243yc; $CH_3CF=CF_2$), and tetrafluoropropane (HFC-1234ze; $CF_3CH=CHF$, HFC-1234yf; $CF_3CF=CH_2$). Patent Document 1 further describes using a mixture of an HFC propene compound and a known HFC compound, such as HFC-32.

The use of an HFC propene compound as a refrigerant is disclosed in Patent Document 2 (WO2004/037913), as well as in Patent Document 1. Patent Document 2 further describes using, as a refrigerant, a combination of a propene HFC compound and a known HFC compound. Patent Document 2 mentions trifluoropropene (HFC-1243zf; $CF_3CH=CH_3$), tetrafluoropropane (HFC-1234ze; $CF_3CH=CHF$, HFC-1234yf; $CF_3CF=CH_2$), and pentafluoropropene (HFC-1225ye; $CF_3CF=CHF$) as examples of propene compounds.

Patent Document 3 (U.S. Patent No. 7,279,451) discloses using HFC-1234yf and HFC-1225ye as refrigerants, and also discloses using a mixture of HFC-32 with HFC-1234yf or HFC-1225ye.

Patent Document 4 (WO 2006/094303) discloses an HFC propene compound, and many mixture compositions containing the HFC propene compound. A combination of HFC-1225ye with HFC-32 is described as one of such mixtures. Patent Document 4 states that the HFC-32 content of the mixture composition is in the range of 1 to 99%, more preferably 1 to 50%, and most preferably 5% or 3%. Patent Document 4 describes HFC-32/HFC-1225ye mixtures having HFC-32 contents of 3%, 5%, 40%, 45%, and 50% in the Examples; however, it nowhere describes whether such mixture compositions are flammable.

As described above, refrigerants containing HFC-1225ye, and refrigerants containing both HFC-1225ye and HFC-32 are already known.

The above-mentioned HFC propene compounds have a global warming potential (GWP) of 10 at most, which is far lower than the GWP of refrigerants in current use, such as HFC134a (GWP: 1300) and R410A (GWP: 2030).

Non-Patent Document 1 (FluoroChemical Catalogue 2004, SynQuest Laboratories, Inc.) states that HFC-1225ye has a boiling point of -18°C, and is flammable.

Patent Document 4 states that HFC-1225ye is nonflammable, but there is no description regarding the flammability of a mixed refrigerant of HFC-1225ye and HFC-32.

HFC-1225ye may exist structurally as geometric isomers, i.e., as a cis-(Z) isomer and a trans-(E) isomer, and methods for producing these isomers are known; however, there is no description stating that these geometric isomers can be used as refrigerants (Non-Patent Document 2: J. Fluorine Chem., 23 (1983) 339, Non-Patent Document 3: J. Fluorine Chem., 44 (1989) 167).

Patent Document 5 (WO 2007/053688) discloses an azeotropic composition containing such geometric isomers and HF. The boiling point of cis-HFC-1225ye is described therein.

Patent Document 1: Japanese Unexamined Patent Publication No.

1992-110388
Patent Document 2: WO 2004/037913
Patent Document 3: U.S. Patent No. 7,279,451
Patent Document 4: WO 2006/094303
Patent Document 5: WO 2007/053688
Non-Patent Document 1: FluoroChemical Catalogue 2004, SynQuest Laboratories, Inc.
Non-Patent Document 2: J. Fluorine Chem., 23 (1983) 339
Non-Patent Document 3: J. Fluorine Chem., 44 (1989) 167

## DISCLOSURE OF THE INVENTION

[PROBLEM TO BE SOLVED BY THE INVENTION]

A principal object of the present invention is to provide: a refrigerant that has little effect on the ozone layer and on global warming (low GWP), is nonflammable, and has refrigerant characteristics substantially equivalent to those of known HFC-134a (for car air conditioners) or R410A (for air conditioners); and a method of operating a refrigerator using the refrigerant.

[MEANS FOR SOLVING THE PROBLEM]

The present inventors carried out extensive research to achieve the above object. As a result, the inventors found that when difluoromethane (HFC-32), which can achieve high refrigerant performance but cannot be used singly because of its extremely high flammability, is mixed with pentafluoropropene (HFC-1225ye), the resulting mixture forms a nonflammable refrigerant, and a mixture containing HFC-1225ye and HFC-32 in specific proportions can achieve refrigeration performance equivalent to that of R410A. The inventors further found that pentafluoropropene containing 90 mol% or more of (Z)HFC-1225ye, which is a geometric isomer having a GWP of not more than 10, can be used as a replacement for HFC-134a in terms of performance, and is a nonflammable refrigerant.

More specifically, the present invention provides the following nonflammable refrigerants, and methods of operating a refrigerator using such refrigerants.

Item 1. A refrigerant comprising HFC-1225ye containing 90 mol% or more of (Z)HFC-1225ye.

Item 2. A refrigerant comprising HFC-1225ye containing 95 mol% or more of (Z)HFC-1225ye.

Item 3. A method of operating a refrigerator using the refrigerant of Item 1 or 2.

Item 4. A mixed refrigerant of HFC-32 and HFC-1225ye containing 90 mol% or more of (Z)HFC-1225ye.

Item 5. A mixed refrigerant of HFC-32 and HFC-1225ye containing 95 mol% or more of (Z)HFC-1225ye.

Item 6. A mixed refrigerant of HFC-32 and HFC-1225ye according to Item 4 or 5, in which the HFC-32 content is 10 to 35 mass%.

Item 7. A mixed refrigerant of HFC-32 and HFC-1225ye according to Item 4 or 5, in which the HFC-32 content is 10 to 25 mass%.

Item 8. A method of operating a refrigerator using the mixed refrigerant of any one of Items 4 to 7.

Item 9. A refrigerant composition comprising a mixed refrigerant of HFC-32 and HFC-1225ye containing 90 mol% or more of (Z)HFC-1225ye, the HFC-32 content in the vapor phase of the mixed refrigerant being not more than 74 mol% (53 mass%) at room temperature.

Item 10. A refrigerant composition according to Item 9 wherein the HFC-1225ye contains 95 mol% or more of (Z)HFC-1225ye.

Item 11. A refrigerant composition according to Item 9 or 10 comprising a refrigerator oil.

Item 12. A refrigerant composition according to Item 11 comprising a drying agent.

Item 13. A refrigerant composition according to Item 11 or 12 comprising a stabilizer.

Item 14. A method of operating a refrigerator using the refrigerant composition of any one of Items 9 to 13.

HFC-1225ye is known to be usable as a refrigerant. For example, Non-Patent Document 1 states that HFC-1225ye has a boiling point of -18°C. HFC-1225ye may exist structurally as geometric isomers called a "Z isomer" (cis isomer) and an "E isomer" (trans isomer). In the present invention, the "HFC-1225ye refrigerant" refers to one of, or a mixture of the geometrical isomers. In the present invention, the inventors synthesized HFC-1225ye by a standard method for producing HFC-1225ye that comprises bringing the starting material HFC-236ea ($CF_3CFHCHF_2$) into contact with a catalyst at 350°C to remove HF.

Gas chromatography analysis confirmed that HFC-1225ye produced under the above-mentioned reaction conditions is a mixture containing 86 mol% of the Z isomer and 14 mol % of the E isomer. Although separating these isomers had been nowhere disclosed, the present inventors found that the mixture can be completely separated into the Z isomer (hereinafter referred to as "(Z)HFC-1225ye") and the E isomer (hereinafter referred to as "(E)HFC-1225ye") by a usual distillation method.

The boiling point of HFC-1225ye currently known is -18°C (FluoroChemical Catalogue 2005, SynQuest Laboratories, Inc.). Patent Document 5 states that the boiling point of (Z)HFC-1225ye is -20°C.

In the patent invention, the inventors determined the vapor pressure-temperature relationships of (Z)HFC-1225ye and (E) HFC-1225ye separated from each other. The results were fitted to the Antoine equation to calculate the boiling points of (Z)HFC-1225ye and (E)HFC-1225ye, which were found to be -19.5°C and -15.3°C, respectively. The boiling point of the E isomer had been nowhere described. The ratio of (Z)HFC-1225ye and (E)HFC-1225ye in the known HFC-1225ye having a boiling point of -18°C was proportionally estimated from the obtained boiling points of (Z)HFC-1225ye and (E)HFC-1225ye. The results indicated that the known HFC-1225ye is a mixture of geometric isomers consisting of 36 mol% of (E)HFC-1225ye and 64 mol% of (Z)HFC-1225ye. Thus, it can be concluded that HFC-1225ye containing more than 64 mol% of (Z)HFC-1225ye was unknown. The measurement results also revealed the boiling point of HFC-1225ye consisting only of (Z)HFC-1225ye is -19.5°C, which is lower than -18°C.

There is a thermal equilibrium between (Z)HFC-1225ye and (E)HFC-1225ye, i.e., geometric isomers of HFC-1225ye. The (Z)HFC-1225ye/(E)HFC-1225ye ratio (molar ratio) is 97/3 at 100°C, 91/9 at 250°C, and 87/13 at 350°C. In other words, as the temperature increases, the proportion of (E)HFC-1225ye in HFC-1225ye increases. The presence of thermal equilibrium indicates that the (E)HFC-1225ye content of the mixture that contains a high proportion, such as 50 mol% or more, of (E)HFC-1225ye may change over time.

The boiling point of the Z isomer is lower than that of the E isomer. A higher Z isomer content is preferable as a low temperature refrigerant. However, if the E isomer content of the mixed refrigerant changes in a refrigerator, the refrigerant performance changes during use, which is not preferable. The temperature in refrigerators is assumed not to exceed 250°C. Thus, if the mixture originally contains 90 mol% or more of the Z isomer, the Z isomer content would not become less than 90 mol%. Further, if the mixture contains 95 mol% or more of the (Z) isomer, the change in the Z isomer content, if any, would have little effect on the refrigerant performance.

HFC-134a, currently used as a refrigerant for car air conditioners, has a boiling point of -26°C. The boiling points of the E isomer and Z isomer of HFC-1225ye obtained by the above measurements are -15.3°C and -19.5°C, respectively. Thus, the Z isomer has a boiling point closer to that of HFC-134a, and is more suitable as a replacement for HFC-134a.

The refrigerating capacity and COP of (Z)HFC-1225ye and (E)HFC-1225ye were determined as described below in Example 1 and Comparative Example 1. The results showed that (Z)HFC-1225ye has a 73% refrigerating capacity and a 100% COP relative to HFC-134a, whereas (E)HFC-1225ye has a 65% refrigerating capacity and a 101% COP relative to HFC-134a.

These results show that (Z)HFC-1225ye is better than (Z)HFC-1225ye as a replacement for HFC134a. By slightly sacrificing the COP, the refrigerating capacity of HFC-1225ye can be increased closer to that of 134a. Patent Document 4 shows HFC-

1225ye/HFC-32 mixed refrigerants (with HFC-32 contents of 3% and 5%) in Table 10. The inventors of the present invention found that the single use of (Z)HFC-1225ye, which is easy to handle and has a low global warming potential, may be also suitable as a replacement for HFC-134a. In this case, the amount of HFC-32 having a high global warming potential can be further reduced, and the global warming potential of the resulting refrigerant can be lowered.

The possible use of conventional HFC-32 as a replacement for the R410A currently used as an air conditioner refrigerant has been studied. However, while HFC-32 has excellent refrigerant performance, it is slightly flammable; because of this major defect, HFC-32 cannot be used singly as a refrigerant.

A prior art publication states that 1225ye, with a boiling point of -18°C, is flammable. However, the present inventors performed measurements (the ASHRAE method) and found that when a mixed refrigerant of (Z)HFC-1225ye and HFC-32 (a HFC-32/HFC-1225ye mixed refrigerant) contains 26 mol% (47 mass%) or more of (Z)HFC-1225ye, the mixed refrigerant is nonflammable. Thus, the inventors found that a nonflammable refrigerant can be produced by mixing (Z)HFC-1225 and HFC-32 in an appropriate ratio. This also indicates that HFC-1225ye is nonflammable.

In the present invention, the relationship between flammability and the mixing ratio of pentafluoropropene ((Z)HFC-1225ye) and difluoromethane (HFC-32) having a flammable range was studied in the following manner. The flammability was determined according to the ASHRAE method (a 10L balloon flask, ignition by discharge, measured at 60°C). The ASHRAE method is described in ASHRAE Standard 34-2001-ASTM Designation; E681.

The results of the flammability measurement revealed that a HFC-32/(Z)HFC-1225ye gas mixture containing 26 mol% or more of (Z)HFC-1225ye is nonflammable.

According to the ASHRAE method, flammability is evaluated based on the risk of the leaked gas mixture composition. The leaked gas mixture composition is evaluated for combustion at a higher temperature selected from either -40°C or the temperature 10K higher than the boiling point of the gas mixture. For example, a HFC-32/(Z)HFC-1225ye mixed refrigerant having a molar ratio of 30/70 is evaluated based on the leaked gas mixture composition (having a HFC-32/(Z)HFC-1225ye molar ratio of 57/43) at -20°C, i.e., a temperature 10K higher than the boiling point of the gas mixture. The present inventors carried out measurements to determine the vapor-liquid equilibrium relationship of an HFC-32/(Z)HFC-1225ye mixed refrigerant. Using the obtained results, the inventors calculated the HFC-32/(Z)HFC-1225ye mixing ratio in the liquid phase at a temperature 10K higher than the boiling point of the mixed refrigerant to achieve an HFC-32/(Z)HFC-1225ye mixing ratio in the vapor phase of 74/26 (mol % ratio), which is the upper limit for nonflammability. The HFC-32/(Z)HFC-1225ye mixing ratio was found to be 44/56 (mol% ratio). The results revealed that a HFC-32/(Z)HFC-1225ye mixed refrigerant containing 56 mol% or more of (Z)HFC-1225ye is nonflammable in both the liquid and vapor phases.

The refrigerant is usually mixed with a refrigerator oil, stabilizer, drying agent, etc., and used as a refrigerant composition in a refrigerator. The refrigerant is required to be nonflammable particularly to avoid the ignition of refrigerant gas leaked from the refrigerator. The flammable HFC-32 content in the vapor phase of the HFC-32/HFC-1225ye mixed refrigerant is higher than that in the liquid phase. Therefore, if the vapor phase of the HFC-32/HFC-1225ye mixed refrigerant is nonflammable, the leaked mixed refrigerant is nonflammable, whether the liquid or vapor phase of the mixture is leaked.

(Z)HFC-1225ye and HFC-32 form a non-azeotropic composition. The HFC-32 content in the vapor phase is clarified after determining the vapor-liquid equilibrium of the refrigerant. A practical HFC-32 content in the vapor phase also becomes clear from the vapor-liquid equilibrium of a refrigerant composition containing the refrigerant, a refrigerator oil, etc. For example, when HFC-32 is more soluble in a refrigerator oil than (Z)HFC-

1225ye, the HFC-32 content is reduced, compared to when using the refrigerant alone. In other words, in the case of using a refrigerator oil, even if the proportion of HFC-32 in the refrigerant is increased, nonflammability can be maintained. Thus, the upper limit for nonflammability is not an HFC content of 44%, but may be further increased, for example, by 10 mol%. (Z)HFC-1225ye and (E)HFC-1225ye are substantially the same in terms of making a HFC-32-containing refrigerant non-flammable.

The temperature 10K higher than the boiling point of the HFC-32/HFC-1225ye mixed refrigerant of the invention is not higher than room temperature. Therefore, if the temperature is increased to room temperature, the HFC-32 content of the vapor phase of the mixed refrigerant is reduced. Thus, if the HFC-32 content in the vapor phase at room temperature is not beyond the upper limit for nonflammability, the refrigerant is completely safe in terms of flammability.

In the HFC-1225ye refrigerant of the invention, HFC-1225ye contains 90 mol% or more, preferably 95 mol%, of (Z)HFC-1225ye. HFC-1225ye containing 99 mol% or more of (Z)HFC-1225ye, i.e., consisting substantially of only (Z)HFC-1225ye, may also be used as the refrigerant. It is also possible to use (Z)HFC-1225ye alone as the refrigerant.

When a mixture of HFC-1225ye and HFC-32 is used as the refrigerant of the invention, the HFC-32 content of the mixed refrigerant (liquid phase) is usually about 10 to about 35 mass%, and preferably about 10 to about 25 mass%. The upper limit of the HFC-32 content depends on the flammability of the mixed refrigerant. When the refrigerant is used alone, the maximum HFC-32 content for nonflammability is 23 mass%. This value of a refrigerant composition containing the refrigerant and a refrigerator oil, stabilizer, or the like varies depending on the solubility of the mixed refrigerant components in such an additive, and thus depends on the kind of additive used. Thus, the starting HFC-32 content in a practical nonflammable refrigerant may be more than 23 mass%. For example, the starting

HFC-32 content may be about 30 mass%; this value depends on the components of the refrigerant composition. The same applies to the use of HFC-1225ye containing at least 90 mol% or at least 95 mol% of (Z)HFC-1225ye.

When using (E)HFC-1225ye that has a boiling point higher than (Z)HFC-1225ye, the refrigerating capacity is reduced. To compensate for the reduction of the refrigerating capacity, it is necessary to increase the proportion of HFC-32.

The global warming potential, GWP, of HFC-32 is about 600, and that of HFC-1225ye is not more than 10. If the HFC-32 content of the mixed refrigerant is halved, the global warming potential thereof can also be substantially halved. The reduction of the HFC-32 content can directly reduce the GWP of the mixed refrigerant. When using a mixed refrigerant containing (Z)HFC-1225ye in place of (E)HFC-1225ye, the HFC-32 content can be reduced for the same refrigerating performance. The use of (Z)HFC-1225ye rather than (E)HFC-1225ye is also preferable from the viewpoint of global warming potential.

The higher the HFC-32 content in a mixture of (Z)HFC-1225ye and HFC-32, the higher the refrigerant capacity. (Z)HFC-1225ye/HFC-32 mixtures having an HFC-32 content of 27 mass% and an HFC-32 content of 15 mass%, respectively and having the same refrigerant capability as known R410A were compared. The comparison reveals that that their COPs during cooling are 95 and 77%, and their COPs during heating are 98 and 84%, respectively. These results show that a mixed refrigerant of (Z)HFC-1225ye and HFC-32 can be used as a substitute for R410A.

The mixture of HFC-1225ye and HFC-32 forms a non-azeotropic composition, and thus has a temperature glide (a temperature difference before and after evaporation). The smaller the temperature glide, the better. A comparison of (Z)HFC-1225ye and (E)HFC-1225ye shows that a mixture of (E)HFC-1225ye with HFC-32 (at the maximum ratio for nonflammability) has a temperature glide of 10K, and a mixture of (Z)HFC-1225ye with HFC-32 (at the maximum ratio for nonflammability) has a temperature glide of 8K, which is lower. Thus, the mixture of (Z)HFC-1225ye and HFC-32 can be more easily handled in a refrigerator.

The HFC-1225ye refrigerant or HFC-1225ye/HFC-32 mixed refrigerant of the invention may be mixed with at least one member selected from the group consisting of R-125, R-134a, R-143a, R-152a, propane, propylene, isobutane, and cyclopropane, and used as a mixed refrigerant. When the mixed refrigerant of HFC-1225ye/HFC-32 is mixed with at least one member selected from the group consisting of R-125, R-134a, R-143a, R-152a, propane, propylene, isobutane, and cyclopropane, the mixing ratio is preferably selected so as to make the liquid and vapor phases of the mixed refrigerant nonflammable.

Examples of refrigerator oils used with the refrigerant of the invention include ester-based refrigerator oils and ether-based refrigerator oils. The ester compound used as an ester-based refrigerator oil reacts easily with water because of its ester structure, and is thus prone to hydrolysis. Therefore, when water enters the system, the ester compound is hydrolyzed to produce carboxylic acid. The carboxylic acid reacts with metals to form insoluble metallic soaps, thus leading to plugged capillaries of the refrigerator. Accordingly, when an ester-based refrigerator oil is used, water must be removed from the system. One of the methods for doing so is removing water from the refrigerator oil using a drying agent such as zeolite. However, some types of zeolites are reactive with HFC-32 and refrigerator oils (ester-based oils, ether-based oils). The reaction increases the total acid value of the refrigeration system, which may result in corrosion and poor performance. Therefore, the drying agent to be used should be carefully selected.

Generally, zeolite is a crystalline aluminosilicate represented by Formula (3)

$$M_{2/n}O \cdot Al_2O_3 \cdot aSiO_2 \cdot bH_2O \quad (3)$$

In Formula (3), M represents a metal cation; n is a valence of the metal cation, and is usually a number from 1 to 2; a is a number from 2 to 10; and b is a number from 2 to 7. Examples of the metal cation include monovalent cations such as Li, Na, K and Cs, and divalent cations such as Mg, Ca, and Ba.

Examples of the zeolite include zeolites containing one or more types of metal cations. When a synthetic zeolite whose average pore diameter is smaller than the molecular diameter of HFC-32, more specifically a synthetic zeolite having an average pore diameter not larger than 3.0Å is used as a drying agent for the working medium, halogenated hydrocarbons containing one carbon atom, such as HFC-32, in the refrigerant are prevented from being adsorbed and decomposed, and coexisting refrigerator oils for lubrication are protected from destabilization.

When a synthetic zeolite whose average pore diameter is larger than the diameter of a water molecule, more specifically a synthetic zeolite having an average pore diameter larger than 2.6 Å, preferably 2.7 Å or more, more preferably 2.8 Å or more, and particularly preferably 2.9 Å or more is used as a drying agent for the working medium, the working medium can be efficiently dehydrated (dried). The average pore diameter of the synthetic zeolite can be determined by the nitrogen adsorption method, observation under an electron microscope (TEM, SEM), or like methods.

In a preferred embodiment, an A-type zeolite containing Na and/or K as a metal cation, more specifically a synthetic zeolite represented by Formula (4), is used.

$$(Na_{1-x} \cdot K_x) \cdot (Al_2O_3) \cdot (2SiO_2) \cdot yH_2O \quad (4)$$

In Formula (4), x is a number from 0 to 1, and y is a number from about 0 to about 6.

The amount of synthetic zeolite to be used is not lower than 0.2 wt. parts, preferably not lower than about 0.5 wt. parts, but not higher than about 3 wt. parts, and preferably not higher than about 2 wt. parts, per wt. part of the working medium circulating inside the refrigerator.

The configuration of the drying agent is not particularly limited. The synthetic zeolite may be used in a powdery, granular or molded form. The shape of the molded zeolite is not particularly limited and may be, for example, cylindrical, prism-shaped, or spherical. Binders may be used to mold the synthetic zeolite.

Usable binders include clay binders and silica binders. Examples of clay binders include kaolin clays. Examples of kaolin clays include kaolin minerals, serpentine minerals, chamosite, amesite, greenalite, cronstedtite, hydrated halloysite, halloysite, kaolinite, dickite, nacrite, chrysotile, antigorite, Zettlitz kaolin, Cornwall kaolin, Georgia kaolin, Hong Kong kaolin, Korean kaolin, Fuzhou clay, Gaerome clay, Seta kaolin, Iwate kaolin, Hijiori kaolin, Ibusuki kaolin, Kanpaku kaolin, and the like. Such kaolins can be used singly or in a combination of two or more types.

The mixing ratio of the binder to the synthetic zeolite is not particularly limited. Generally, the proportion of the binder to the synthetic zeolite is not lower than 1 wt.%, preferably not lower than 10 wt.%, more preferably not lower than 20 wt.%, but not higher than 50 wt.%, preferably not higher than 40 wt.%, and more preferably not higher than 30 wt.%.

Used as the refrigerator oil is an ether-based refrigerator oil (an ether compound having at least one ether bonding group) or an ester-based refrigerator oil (an ester compound having at least one ester bonding group), preferably a refrigerator oil based on the ester having 9 or more carbon atoms or a refrigerator oil based on the ether having 10 or more carbon atoms.

Examples of the ether-based refrigerator oil include alkyl ethers of polyglycols having oxyethylene units and/or oxypropylene units. Specific examples thereof are compounds represented by the following Formula (1) or (2):

$R^1$-O-X$R^2$ (1)

$CH_2$-OX-$R^3$
|
CH-O-X-$R^4$ (2)
|
$CH_2$-O-X-$R^5$

In Formulas (1) and (2), X represents a (co)polymer unit of ethylene oxide and/or propylene oxide. In Formula (1), $R^1$ and $R^2$ are the same or different and each represent an alkyl group having 1 to 4 carbon atoms (methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, t-butyl).

In Formula (2), $R^3$, $R^4$, and $R^5$ are the same or different and each represent a hydrogen atom or an alkyl group having 1 to 4 carbon atoms (methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, t-butyl).

Examples of the ester-based refrigerator oil include polyol esters synthesized by intermolecular dehydration of a straight- or branched-chain fatty acid having 2 to 9 carbon atoms, and an aliphatic polyhydric alcohol having 2 to 6 carbon atoms. Examples of the fatty acid include methylhexanoic acid, n-heptanoic acid, trimethylhexanoic acid, and the like. Examples of the polyhydric alcohol include pentaerythritol, trimethylolpropane, neopentylglycol, and the like. The amount of refrigerator oil to be added to the refrigerant is about 0.5 to about 3 wt. parts, per wt. part of the refrigerant.

The nonflammable refrigerant of the invention has high stability. If necessary, stabilizers may be added to meet the requirement of high stability under severe conditions.

Examples of such stabilizers include (i) aliphatic nitro compounds such as nitromethane and nitroethane; aromatic nitro compounds such as nitrobenzene and nitrostyrene; (ii) ethers such as 1,4-dioxane; amines such as 2,2,3,3,3-pentafluoropropylamine and diphenylamine; butylhydroxyxylene, benzotriazole, etc.

The stabilizer contains at least one type of compound selected from the above compounds (i), and may optionally contain at least one type of compound selected from the above compounds (ii).

The amount of stabilizer used may be any amount that does not impair the performance of the nonflammable composition, although it may vary depending on the type of stabilizer used. In general, the stabilizer is preferably used in an amount of about 0.1 to about 10 wt. parts, and more preferably about 0.1 to about 5 wt. parts, per 100 wt. parts of the composition.

[EFFECT OF THE INVENTION]

The refrigerant of the invention has the following excellent characteristics.

(1) Pentafluoropropene contained in the refrigerant of the invention does not contain chlorine or bromine. Therefore, even if the refrigerant of the invention is emitted into the atmosphere, there is no risk of ozone layer depletion.

(2) Pentafluoropropene contained in the refrigerant of the invention has a low global warming potential (GWP). Thus, the refrigerant of the invention has little effect on global warming.

(3) Pentafluoropropene contained in the refrigerant of the invention is nonflammable. Therefore, a nonflammable refrigerant can be produced.

(4) The refrigerant of the invention has refrigerant characteristics equivalent to those of known HFC-134a (for car air conditioners) or R410A (for air conditioners). Therefore, the refrigerant is suitable for various uses.

## BEST MODE FOR CARRYING OUT THE INVENTION

[EXAMPLES]

The following Examples and Comparative Examples are provided to illustrate the present invention in further detail, but are not intended to limit the scope of the invention.

### Example 1

The refrigerant capacity of (Z)HFC1225ye and HFC134a was determined using a calorimeter at an evaporation temperature of 5°C and a condensation temperature of 50°C, with degrees of supercooling and superheating of 5°C. The refrigerating capacities of (Z)HFC1225ye and HFC134a were 1,712 kJ/$m^3$ and 2,360 kJ/$m^3$, respectively; and the COPs thereof were nearly equal, at about 5.0. It was revealed that (Z)HFC1225ye alone has a 73% refrigerating capacity relative to HFC134a. The capacity is presumably further increased by sacrificing the COP.

Comparative Example 1

The refrigerant capacity was determined in the same manner as Example 1, except that (E)HFC1225ye was used in place of (Z)HFC1225ye or HFC134a. As a result, the refrigerating capacity was 1,539 kJ/$m^3$, and the COP was 5.1. The refrigerating capacity of (E)HFC1225ye was 90% relative to that of (Z)HFC1225ye, and 65% relative to that of HFC134a.

Example 2

Mixed gases of (Z)HFC1225ye and HFC32 with various ratios were placed in 10 L spherical flasks and maintained at 60°C. According to ASHRAE STANDARD 34-2001 ASTM Designation E681, the mixed gases were ignited by discharge (15 kV, 30 mA), and the flammability or non-flammability was determined by observing the spread of flame at that time. As a result, it was confirmed that (Z)HFC1225ye/HFC32 mixed gases in which the HFC32 content was 74 mol% (53 mass%) or less were non-flammable.

Example 3

Mixed refrigerants of HFC32 and (Z)HFC1225ye were prepared in 100 ml autoclaves and maintained at 25°C. Taking the liquid phase ratio as the starting ratio, the gaseous phase ratio was determined using a gas chromatograph calibrated beforehand. As a result, when the liquid phase ratio was HFC32/(Z)HFC1225ye=50.6/49.4 (mol ratio), the gaseous phase ratio was HFC32/(Z)HFC1225ye=78/22 (-24.6°C). When the liquid phase ratio was HFC32/(Z)HFC1225ye=26.7/73.3 (mol ratio), the gaseous phase composition was HFC32/(Z)HFC1225ye=59.8/40.2 (-25°C).

According to the ASHRAE method, the starting ratio that results in the limit ratio for nonflammability determined in

Example 2 was determined at a temperature 10K higher than the boiling point of each mixed gas using vapor-liquid equilibrium measurements, and found to be HFC32/(Z)HFC1225ye=44/56 (mol ratio) or 23/77 (mass ratio). The above demonstrates that when the HFC32 content in a HFC32/(Z)HFC1225ye mixed refrigerant (liquid phase) is 23 mass% or less, both the liquid phase and gaseous phase of the mixed refrigerant have non-flammability, as determined by the ASHRAE method. The measurement of the non-flammable range revealed that non-flammable refrigerants that can replace R410A can be formed.

Example 4

Real machine tests were conducted using refrigerants with two ratios. Real machines were operated under cooling conditions of 27°C/19°C for the indoor units and 35°C/24°C for the outdoor units, and heating conditions of 20°C/12°C for the indoor units and 7°C/6°C for the outdoor units, using 1,250 g of a HFC32/(Z)HFC1225ye mixed refrigerant (weight ratio = 27/73 or 15/85) or R410A (HFC32/HFC125=50/50 (mass ratio)), so as to exhibit the same refrigerating capacity as R410A; the COP at that time was calculated. Table 1 shows the results.

Table 1

| | Heating COP | Heating COP relative to R410A | Cooling COP | Cooling COP relative to R410A |
|---|---|---|---|---|
| HFC32/(Z)HFC1225ye=27/73 | 2.86 | 98% | 3.03 | 95% |
| HFC32/(Z)HFC1225ye=15/85 | 2.46 | 84% | 2.45 | 77% |

Although a decreased HFC32 content reduces the COP, even a refrigerant HFC32/(Z)HFC1225ye weight ratio of 15/85 exhibited a COP of about 80% relative to R410A. Further, it was revealed that a HFC32/(Z)HFC1225ye weight ratio of about 27/73 achieves performance substantially equivalent to R410A.

Comparative Example 2

The COP was determined in the same manner as in Example 4, except that (E)HFC1225ye was used in place of (Z)HFC1225ye, and the refrigerant HFC32/HFC1225ye weight ratio was 27/73. Table 2 shows the results.

Table 2

| | Heating COP | Heating COP relative to R410A | Cooling COP | Cooling COP relative to R410A |
|---|---|---|---|---|
| HFC32/(E)HFC1225ye=27/73 | 2.63 | 90% | 2.62 | 82% |

Tables 1 and 2 demonstrate that the use of (Z)HFC1225ye achieves higher refrigerant capacity than the use of (E)HFC1225ye.

Example 5

The pressure-temperature relationship was determined in (E)HFC1225ye and (Z)HFC1225ye with 99% or higher purity, from which low boiling substances had been removed. The results were fitted to the Antoine equation to calculate the boiling points of (E)HFC1225ye and (Z)HFC1225ye, which were found to be -15.3°C and -19.5°C, respectively.

CLAIMS

1. A refrigerant comprising HFC-1225ye containing 90 mol% or more of (Z)HFC-1225ye.

2. A refrigerant comprising HFC-1225ye containing 95 mol% or more of (Z)HFC-1225ye.

3. A method of operating a refrigerator using the refrigerant of claim 1 or 2.

4. A mixed refrigerant of HFC-32 and HFC-1225ye containing 90 mol% or more of (Z)HFC-1225ye.

5. A mixed refrigerant of HFC-32 and HFC-1225ye containing 95 mol% or more of (Z)HFC-1225ye.

6. A mixed refrigerant of HFC-32 and HFC-1225ye according to Claim 4 or 5, in which the HFC-32 content is 10 to 35 mass%.

7. A mixed refrigerant of HFC-32 and HFC-1225ye according to claim 4 or 5, in which the HFC-32 content is 10 to 25 mass%.

8. A method of operating a refrigerator using the mixed refrigerant of any one of claims 4 to 7.

9. A refrigerant composition comprising a mixed refrigerant of HFC-32 and HFC-1225ye containing 90 mol% or more of (Z)HFC-1225ye, the HFC-32 content in the vapor phase of the mixed refrigerant being not more than 74 mol% (53 mass%) at room temperature.

10. A refrigerant composition according to claim 9 wherein the HFC-1225ye contains 95 mol% or more of (Z)HFC-1225ye.

11. A refrigerant composition according to claim 9 or 10 comprising a refrigerator oil.

12. A refrigerant composition according to claim 11 comprising a drying agent.

13. A refrigerant composition according to claim 11 or 12 comprising a stabilizer.

14. A method of operating a refrigerator using the refrigerant composition of any one of claims 9 to 13.

# INTERNATIONAL SEARCH REPORT

International application No
PCT/JP2008/070641

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

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 practical, search terms used)

EPO-Internal, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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

[X] See patent family annex.

* Special categories of cited documents :

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"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 |
|---|---|
| 9 March 2009 | 16/03/2009 |

| Name and mailing address of the ISA/ | Authorized officer |
|---|---|
| European Patent Office, P.B. 5818 Patentlaan 2<br>NL – 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040,<br>Fax: (+31-70) 340-3016 | Puetz, Christine |

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