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(73) Patenthaver: **DAIKIN INDUSTRIES, LTD., Umeda Center Building, 4-12, Nakazaki-nishi 2-chome, Kita-ku, Osaka-shi, Osaka 530-8323, Japan**

(72) Opfinder: **Takahashi, Kazuhiro, c/o DAIKIN INDUSTRIES, LTD., Umeda Center Building, 4-12, Nakazaki-Nishi 2-chome, Kita-ku, Osaka-shi, Osaka 530-8323, Japan**
Tsuchiya, Tatsumi, c/o DAIKIN INDUSTRIES, LTD., Umeda Center Building, 4-12, Nakazaki-Nishi 2-chome, Kita-ku, Osaka-shi, Osaka 530-8323, Japan
Yamada, Yasufu, c/o DAIKIN INDUSTRIES, LTD., Umeda Center Building, 4-12, Nakazaki-Nishi 2-chome, Kita-ku, Osaka-shi, Osaka 530-8323, Japan

(74) Fuldmægtig i Danmark: **Dennemeyer & Associates S.A, P.O. Box 700425, DE-81304 Munich, Tyskland**

(54) Benævnelse: **HALOGENOLEFINBASERET SAMMENSÆTNING OG ANVENDELSE DERAF**

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DESCRIPTION

Technical Field

[0001] The present invention relates to a haloolefin-based composition and use thereof.

Background Art

[0002] Hydrofluorocarbons (HFCs), such as HFC-125 and HFC-32, have been widely used as important substitutes for e.g. CFCs and HCFCs which are known as substances that deplete the ozone layer. Known examples of such substitutes include "HFC-410A," which is a mixture of HFC-32 and HFC-125, "HFC-404A," which is a mixture of HFC-125, HFC-134a and HFC-143a.

[0003] Such substitutes have various applications, such as heat transfer media, refrigerants, foaming agents, solvents, cleaning agents, propellants, and fire extinguishers, and are consumed in large amounts. However, since these substances have a global warning potential (GWP) several thousand times higher than that of CO_2, many people are concerned that their diffusion may affect global warming. As a global warming countermeasure, the substances are collected after being used; however, not all of them can be collected, and their diffusion due to leakage cannot be disregarded. For use in e.g. refrigerants and heat transfer media, although substitution with CO_2 or hydrocarbon-based substances has been studied, CO_2 refrigerants have many difficulties in reducing comprehensive greenhouse gas emissions, including energy consumption, because of the requirement of large equipment due to the low efficiency of the CO_2 refrigerants. Hydrocarbon-based substances also pose safety problems due to their high flammability.

[0004] Hydrofluoroolefins with a low warming potential are recently attracting attention as substances that can solve these problems. Hydrofluoroolefin is a generic name for unsaturated hydrocarbons containing hydrogen, fluorine, and chlorine, and includes substances represented by the following chemical formulae. The description in parentheses following each chemical formula indicates the refrigerant number typically used for refrigerant purposes.

$CF_3CF{=}CF_2$ (HFO-1216yc or hexafluoropropene),

$CF_3CF{=}CHF$ (HFO-1225ye),

$CF_3CF{=}CH_2$ (HFO-1234yf),

$CF_3CH{=}CHF$ (HFO-1234ze),

$CF_3CH{=}CH_2$ (HFO-1243zf)

$CF_3CCl=CH_2$ (HCFO-1233xf),

$CF_2ClCC1=CH_2$ (HCFO-1232xf),

$CF_3CH=CHCl$ (HCFO-1233zd),

$CF_3CCl=CHCl$ (HCFO-1223xd),

$CClF_2CCl=CHCl$ (HCFO-1222xd),

$CFCl_2CCl=CH_2$ (HCFO-1231xf), and

$CH_2ClCCl=CCl_2$ (HCO-1230xa) .

[0005] Of these, fluoropropenes are particularly promising substances as candidates for refrigerants or heat transfer media with a low GWP; however, they may sometimes gradually decompose over time, and thus are not highly stable. Accordingly, these substances have a problem of gradually reducing performance depending on the situation or environment when used in various applications.

[0006] To enhance the stability of fluoropropenes, a method for adding a phenol compound to a composition containing HFO-1234yf and CF_3I is known (see, for example, WO2005/103187.

[0007] N.D. Rohatgi et al, AHRTI Report No. 09004-01, March 2012 discloses in section 3.1 experiments on the ageing/decomposition of mixtures of HFO-1234yf with equal amounts (mass) of ISO 32 Mixed Acid, ISO 32 Branched Acid or PVE 32-A lubricant in sealed glass tubes, wherein the lubricant had an initial water content of about 500 ppm, the initial air content in the tube was about 2000 ppm, and coupons of steel, aluminum or copper were immersed in the mixtures. The sealed tubes were aged for 14 days at 175°C and then analyzed. The results are summarized in Tables 20-28 of the report.US-A-2013/0099154 discloses compositions comprising HFO-1234ze and polyol ester (POE) lubricants having low moisture and air/oxygen contents and are suitable as heat transfer fluids in refrigeration, heat transfer and air conditioning.

Summary of Invention

Technical Problem

[0008] The above method can improve the stability of HFO-1234yf by the effect of the phenol compound; however, it still has a problem of handling difficulty during mixing. The method for improving stability by adding a phenol compound as described above may also reduce the performance of fluoropropenes by the effect of the phenol compound, and has a problem in improving stability while maintaining performance.

[0009] The present invention was accomplished based on the above, and an object of the present invention is to provide a haloolefin-based composition comprising a highly-stable haloolefin in which decomposition and oxidization are inhibited, and the haloolefin-based composition being used in a heat transfer medium, refrigerant, foaming agent, solvent, cleaning agent, propellant, or fire extinguisher. Another object of the present invention is use of the highly stable haloolefin-based composition in a heat transfer medium, refrigerant, foaming agent, solvent, cleaning agent, propellant, or fire extinguisher.

Solution to Problem

[0010] As a result of extensive research to achieve the above object, the present inventors found that the above object can be attained by using a composition containing a haloolefin and water, and accomplished the invention. Specifically, the present invention relates to a haloolefin-based composition suitable for use for at least one application selected from heat transfer media, refrigerants, foaming agents, solvents, cleaning agents, propellants, and fire extinguishers, which composition comprises

1. (i) a haloolefin, which haloolefin is 2,3,3,3-tetrafluoropropene containing 0.1 to < 10,000 mass ppm of 1,3,3,3-tetrafluoropropene; and, based on the total amount of the haloolefin,
2. (ii) 0.1-200 mass ppm of water; and
3. (iii) ≤ 0.35 mol% of oxygen.

[0011] Also, the present invention relates to the use of the above composition for least one application selected from heat transfer media, refrigerants, foaming agents, solvents, cleaning agents, propellants, and fire extinguishers.

[0012] Preferred embodiments of the invention are as defined in the appended dependent claims and/or in the following detailed description.

Advantageous Effects of Invention

[0013] The present haloolefin-based composition is used for at least one application selected from heat transfer media, refrigerants, foaming agents, solvents, cleaning agents, propellants, and fire extinguishers, and contains water as an essential component. Because the composition contains water, the stability of haloolefin is improved. Specifically, since the double bond in the molecule of the haloolefin can be stably present, and the haloolefin does not easily cause oxidization, the performance of the haloolefin is not likely to be lost for a long period of time. Accordingly, since the composition can provide suitable performance as a heat transfer medium, refrigerant, foaming agent, solvent, cleaning agent, propellant, or fire extinguisher, it is suitable for any of these applications.

[0014] Further, in the present invention, the haloolefin-based composition containing a haloolefin and water is used as a heat transfer medium, refrigerant, foaming agent, solvent, cleaning agent, propellant, and fire extinguisher. As described above, since the haloolefin in the haloolefin composition is stable, performance is not likely to reduce. Accordingly, the composition is suitable for any of applications, including a heat transfer medium, refrigerant, foaming agent, solvent, cleaning agent, propellant, and fire extinguisher.

Description of Embodiments

[0015] Hereinafter, the embodiments of the present invention are explained in detail.

[0016] The haloolefin-based composition used for at least one application selected from heat transfer media, refrigerants, foaming agents, solvents, cleaning agents, propellants, and fire extinguishers (hereinbelow, referred to as "composition") comprises at least haloolefin and water.

[0017] Because the composition contains water as an essential component, the double bond in the molecule of the haloolefin can be stably present, and oxidization of the haloolefin does not easily occur. As a result, the stability of the haloolefin is improved.

[0018] The haloolefin is 2,3,3,3-tetrafluoropropene (HFO-1234yf) containing 0.1 to < 10,000 mass ppm of 1,3,3,3-tetrafluoropropene (HFO-1234ze).

[0019] The haloolefin produced by a known method can be used. One such example includes a method for subjecting fluoroalkane to dehydrofluorination in the presence of a catalyst (a method described, for example, in JP-A-2012-500182). Specifically, as the haloolefin is 2,3,3,3-tetrafluoropropene (HFO-1234yf), 1,1,1,2,3-pentafluoropropane and/or 1,1,1,2,2-pentafluoropropane are used as starting materials, and subjected to dehydrofluorination reaction in the presence of a catalyst to produce 2,3,3,3-tetrafluoropropene (HFO-1234yf).

[0020] In the production of HFO-1234yf according to the above method, a byproduct may also be produced in addition to the target haloolefin. In this case, the resulting product may be purified to remove the byproduct to obtain target HFO-1234yf with high purity. Alternatively, haloolefin may be obtained in the state containing the byproduct without performing purification or by reducing the purity of purification. For example, when HFO-1234yf is produced according to the above production method, E- and Z-isomers of HFO-1234zef, etc., are produced as byproducts. In this case, the byproducts may be removed by purifying the resulting product to obtain the target HFO-1234yf with high purity, or E- and Z-isomers of HFO-1234ze may be contained as byproducts. Accordingly, when the haloolefin is produced by dehydrofluorinating fluoroalkane in the presence of a catalyst, it may contain a byproduct. In the above production method, chromium catalysts, such as chromium oxide or fluorinated chromium oxide, and other metal catalysts can be used as catalysts, and the reaction can be performed at a temperature of 200-500°C.

[0021] The amount of the byproduct is preferably 0.1 to < 10,000 mass ppm based on the total weight of haloolefin, and the haloolefin stabilizing effect may not be significantly inhibited when the amount of the byproduct is in this range.

[0022] Water is not particularly limited, and purified water, such as distilled water, ion exchange water, filtered water, tap water, and ultrapure water obtained by a commercially available device for generating pure water can be used. However, since water containing acid, such as HCl, may corrode equipment or reduce the haloolefin stabilizing effect, it is preferable to remove HCl, etc., to an undetectable level in a typical analysis method. The amount of acid is preferably ≤ 10 mass ppm, and more preferably ≤ 1 mass ppm based on the total amount of the haloolefin, water, and byproduct in the composition.

[0023] Although the pH of the water is not particularly limited, it is generally in the range of 6-8. When the amount of acid in the water is in the above range, the pH of the water is generally within the range of 6-8.

[0024] The amount of water in the composition is preferably ≤ 200 mass ppm based on the total amount of the haloolefin. In this range, the haloolefin stabilizing effect is fully exhibited. The amount of water being ≤ 200 mass ppm, and more preferably < 30 mass ppm based on the total amount of haloolefin can easily prevent device corrosion and the acceleration of haloolefin decomposition. The lower limit of the amount of water in the composition is not limited as long as the effect of the present invention is exhibited. For example, it is 0.1 mass ppm, and more preferably 3 mass ppm. When the amount of water is in this range, the stability of haloolefin in the composition is further improved.

[0025] The amount of water in the composition is particularly preferably > 3 mass ppm and < 30 mass ppm. In this range, the stability of haloolefin in the composition is further improved. The amount of water in the composition being < 30 mass ppm inhibits prevention of refrigerant performance.

[0026] When the byproduct is also produced in the production of haloolefin, the amount of the byproduct in the composition is preferably 0.1 to < 10,000 mass ppm based on the total amount of haloolefin. In this range, the haloolefin stabilizing effect can be sufficiently exhibited.

[0027] The composition may contain other known additives as long as the effect of the present invention is not inhibited. The amount of other additives is preferably ≤ 50 mass%, and more preferably ≤ 40 mass% based on the total amount of the composition.

[0028] The composition can be prepared by any method. For example, each component is prepared and mixed in a predetermined composition ratio, thus obtaining a composition.

[0029] In the composition, because of the presence of water, the double bond of haloolefin is stably present, which is not likely to cause oxidization, attaining highly stable haloolefin. Accordingly, the composition can be stored for a long period of time as compared with typical haloolefins. Moreover, because of the highly stable haloolefin, the performance of haloolefin may not be significantly impaired. Accordingly, the composition can provide stable performance as a heat transfer medium, refrigerant, foaming agent, solvent, cleaning agent, propellant, or fire extinguisher. Specifically, since decomposition or oxidization of haloolefin is not likely to occur, reduced performance in various applications is not likely to be reduced, thus, stable performance can be maintained even after a long period of time. Accordingly, the composition can provide excellent functions when used for any of the applications, including a heat transfer medium, refrigerant, foaming agent, solvent, cleaning agent, propellant, and fire extinguisher.

[0030] The composition can further contain oxygen. The amount of the oxygen is ≤ 0.35 mol% based on the total amount of the haloolefin. When the amount of oxygen is in this range, the stability of haloolefin in the composition is further improved. From this point of view, a lower amount of oxygen in the composition is better. However, as described above, since the composition contains water, the stability of the haloolefin can be maintained by the effect of the water, as long as the amount of oxygen is in the above range. The lower limit of the amount of oxygen in the composition is, for example, 1 ppm, which is the detection limit of gas chromatography.

[0031] Haloolefin has been used as a heat transfer medium, refrigerant, foaming agent, solvent, cleaning agent, propellant, or fire extinguisher. Since the haloolefin in the composition has particularly excellent stability, the composition is especially suitable for any of these applications.

[0032] When the composition is used as a refrigerant or a heat transfer medium, at least either, or both, of polyalkyleneglycol and polyolether can be contained as a lubricating oil in the composition. In this case, the amount of the lubricating oil is 10-50 mass% based on the total amount of haloolefin, water, and byproduct in the composition; however, it is not particularly limited to this range because it differs depending on the specification of the freezer oil tank. When the amount of lubricating oil is in this range, the stability of haloolefin is not impaired. Moreover, the lubricating oil may further contain polyvinyl ether (PVE), or may be formed of polyvinyl ether alone.

[0033] Examples of polyalkyleneglycol (PAG) include "SUNICE P56," produced by Japan Sun Oil Company Ltd. Examples of polyolether (POE) include "Ze-GLES RB32," produced by JX Nippon Oil & Energy Corporation.

[0034] The conventional refrigerant or heat transfer medium that mainly contains haloolefin is likely to cause decomposition or oxidization when it is in contact with e.g. metal, and is likely to lose performance as a refrigerant or heat transfer medium. However, when the above composition is used as a refrigerant or heat transfer medium, a reduction in the performance can be inhibited because of the high stability of the haloolefin.

Examples

[0035] The present invention is explained in detail below with reference to the Examples.

Example 1

[0036] 2,3,3,3-Tetrafluoropropene (HFO-1234yf) and water were prepared and mixed to produce three types of haloolefin-based compositions containing water in amounts of 10 mass ppm and 200 mass ppm relative to the HFO-1234yf. The HFO-1234yf was produced by the method described in Example 1 of JP-A-2012-500182 and JP-A-2009-126803. HF generated in the above production was deoxidized by using a water washing column and an alkali column containing an NaOH aqueous solution. The resulting haloolefin-based composition might contain a byproduct (for example, 1,3,3,3-tetrafluoropropene) generated in the production of HFO-1234yf.

Comparative Example 1

[0037] A haloolefin-based composition was obtained by the same method as in Example 1 except that water was not added, or water was added in an amount of 10,000 mass ppm relative to the HFO-1234yf.

Haloolefin Stability Test 1

[0038] The haloolefin-based compositions obtained in Example 1 and Comparative Example 1 were subjected to a haloolefin stability test as described below. The haloolefin-based composition was added in a manner such that the amount of haloolefin was 0.01 mol to a glass tube (ID 8 mm Φ × OD 12 mm Φ × L 300 mm), a side of which was sealed. The tube was hermitically sealed. The tube was allowed to stand in a constant temperature bath in a 150°C atmosphere, and was kept for one week in this state. Subsequently, the tube was removed from the constant temperature bath and cooled, and then acid in the gas inside the tube was analyzed to evaluate the stability of the haloolefin.

Haloolefin Stability Test 2

[0039] The haloolefin-based compositions obtained in Example 1 and Comparative Example 1 were subjected to a haloolefin stability test as described below. The haloolefin-based composition was added in a manner such that the amount of haloolefin was 0.01 mol to a glass tube (ID 8 mm Φ × OD 12 mm Φ × L 300 mm), a side of which was sealed. Subsequently, oxygen was enclosed in the tube by adjusting. The tube was allowed to stand in a constant temperature bath in a 150°C atmosphere, and was kept for one week in this state. Subsequently, the tube was removed from the constant temperature bath and cooled, and then acid in the gas inside the tube was analyzed to evaluate the stability of the haloolefin.

[0040] Acid in the gas was analyzed according to the following method. Gas remaining in the tube after cooling was completely coagulated by using liquid nitrogen. Subsequently, the tube was opened and gradually defrosted to collect gas in a sampling bag. 5 g of pure water was poured into the sampling bag, and acid was extracted into the pure water while efficiently bringing the pure water into contact with the collected gas. The extract was detected by ion chromatography, and the amounts (mass ppm) of fluoride ions (F-) and trifluoroacetate ions ($CF3COO^-$) were measured.

[0041] Table 1 shows the test results. In Table 1, "yf" and "ze (E)" respectively indicate "HFO-1234yf" and "HFO-1234ze". (E) in "ze (E)" indicates the E isomer of HFO-1234ze. "Ex-" means "Example" and "CE-" means "Comparative Example"

Table 1

No.		Amount of oxygen (mol%)	Amount of water (mass ppm)	Amount of Acid (mass ppm)	
				F^-	CF_3COO^-
1	CE-1	0	0 (N.D.)	<1	<1
2	Ex-1	0	10	<1	<1
3	Ex-1	0	200	<1	<1
4	CE-1	0	10000	<1	<1
5	CE-1	0.010	0 (N.D.)	70	550
6	Ex-1	0.010	10	35	90
7	Ex-1	0.010	200	10	25
8	CE-1	0.010	10000	<1	10
9	CE-1	0.115	0 (N.D.)	300	1850
10	Ex-1	0.115	10	100	330
11	Ex-1	0.115	200	30	100
12	CE-1	0.115	10000	3	20
13	CE-1	0.345	0 (N.D.)	1005	5850
14	Ex-1	0.345	10	330	1900

No.		Amount of oxygen (mol%)	Amount of water (mass ppm)	Amount of Acid (mass ppm)	
				F^-	CF_3COO^-
15	Ex-1	0.345	200	110	675
16	CE-1	0.345	10000	50	275

[0042] The amount of oxygen in each of composition 5-8 in Table 1 was set to 0.010 mol%. Since composition 5 did not contain water, the amount of acid 5 was larger in composition 6-8 containing water. This indicates that since the amount of acid in composition 5 was larger, the decomposition or oxidization of HFO-1234yf, which was a haloolefin, advanced as compared to composition 6-8. The results indicate that HFO-1234yf, which was a haloolefin, was stabilized in the compositions containing water. The amount of oxygen in each of composition 9-12 was 0.115 mol%, and the amount of oxygen in each of composition 13-16 was 0.345 mol%; however, the results of composition 13-16 showed a similar tendency to the results obtained when the amount of oxygen added was 0.115 mol%. In composition 1-4 the amount of acid was below 1 mass ppm, and it was found that most of the haloolefin decomposition did not proceed. This was presumably because oxygen was not added to the system, causing no oxidization. Accordingly, in the system containing substantially no oxygen, the haloolefin was always stable regardless of whether water was contained in the composition.

[0043] The above clearly indicates that water contained in the composition stabilizes haloolefin as in the present invention. This indicates that the composition can provide excellent performance as a heat transfer medium, refrigerant, foaming agent, solvent, cleaning agent, propellant, or fire extinguisher, and the performance can be stably maintained. Accordingly, the composition is suitable for any of the applications, including a heat transfer medium, refrigerant, foaming agent, solvent, cleaning agent, propellant, and fire extinguisher.

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HALOGENOLEFINBASERET SAMMENSÆTNING OG ANVENDELSE DERAF

PATENTKRAV

1. Halogenolefinbaseret sammensætning, der er egnet til anvendelse til mindst en applikation valgt blandt varmeoverførselsmedier, kølemidler, skumdannende midler, opløsningsmidler, rengøringsmidler, drivmidler og brandslukningsmidler, hvilken sammensætning omfatter
   (i) en halogenolefin, hvilken halogenolefin er 2,3,3,3-tetrafluorpropen, der indeholder 0,1 til < 10.000 masse-ppm af 1,3,3,3- tetrafluorpropen; og, baseret på den samlede mængde af halogenolefinen,
   (ii) 0,1-200 masse-ppm af vand og
   (iii) ≤ 0,35 mol-% af oxygen.

2. Sammensætning ifølge krav 1, der yderligere omfatter mindst den ene eller begge af polyalkylenglycol og polyolether i sin egenskab af en smøreolie.

3. Anvendelse af sammensætningen ifølge krav 1 eller 2 til mindst en applikation valgt blandt varmeoverførselsmedier, kølemidler, skumdannende midler, opløsningsmidler, rengøringsmidler, drivmidler og brandslukningsmidler.