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(54) **Titre : COMPOSITION D'HUILE DE LUBRIFICATION POUR DES REFRIGERATEURS ET DES COMPRESSEURS UTILISANT LA COMPOSITION**

(54) **Title: LUBRICATING OIL COMPOSITION FOR REFRIGERATORS AND COMPRESSORS USING THE COMPOSITION**

(57) **Abrégé/Abstract:**
A lubricating oil composition for refrigerators comprising a base oil which comprises as a main component a polyoi ester compound obtained from a polyhydric alcohol selected from among pentaerythritol, dipentaerythritol, trimethylolpropane, and neopentyl glycol and a C_4 to C_{20} aliphatic monocarboxylic acid and which has an acid value of 0.02 mgKOH/g or less and a hydroxyl value of 5 mgKOH/g or less. A compressor using the lubricating composition. The lubricating oil composition is applicable to such refrigerators that use a refrigerant having a specific structure, such as an unsaturated fluorinated hydrocarbon compound, and being usable in current car air conditioner systems, and has excellent compatibility with the refrigerant, good sealing properties, capability of imparting a low coefficient of friction to sliding members and, yet, excellent stability. The compressor uses the lubricating composition.

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Abstract

A lubricating oil composition for refrigerators comprising a base oil which comprises as a main component a polyol ester compound obtained from a polyhydric alcohol selected from among pentaerythritol, dipentaerythritol, trimethylolpropane, and neopentyl glycol and a C_4 to C_{20} aliphatic monocarboxylic acid and which has an acid value of 0.02 mgKOH/g or less and a hydroxyl value of 5 mgKOH/g or less. A compressor using the lubricating composition. The lubricating oil composition is applicable to such refrigerators that use a refrigerant having a specific structure, such as an unsaturated fluorinated hydrocarbon compound, and being usable in current car air conditioner systems, and has excellent compatibility with the refrigerant, good sealing properties, capability of imparting a low coefficient of friction to sliding members and, yet, excellent stability. The compressor uses the lubricating composition.

SPECIFICATION

LUBRICATING OIL COMPOSITION FOR REFRIGERATORS AND COMPRESSORS WITH THE COMPOSITION

[Technical Field]

[0001]

The present invention relates to a lubricating oil composition for refrigerators and, more specifically, to a lubricating oil composition for refrigerators which comprises a base oil comprising a specific polyol ester compound as a main component and which is used for refrigerators using a specific refrigerant, such as an unsaturated fluorinated hydrocarbon compound, having a low global warming potential and being particularly usable in current car air conditioner systems, and to a compressor using such a lubricating oil composition.

[Background Art]

[0002]

A compression-type refrigerator is generally comprised of at least a compressor, a condenser, an expansion mechanism (such as an expansion valve), and an evaporator or comprised additionally of a dryer, and is constructed such that a mixed liquid composed of a refrigerant and a lubricating oil (refrigerator oil) is circulated through a closed system comprising these devices. In such a compression-type refrigerator, in general, a high temperature is established within a compressor while a low temperature is established within a cooler, though depending upon the devices used.

Therefore, it is necessary that the refrigerant and the lubricating oil can be circulated through the system without causing a phase separation in a wide temperature range encompassing from the low temperature to the high temperature. In general, the refrigerant and lubricating oil have temperature regions on a low temperature side and on a high temperature side in which they cause phase separation. The highest temperature in the low temperature side separation region is preferably -10°C or lower, particularly preferably -20°C or lower. On the other hand, the lowest temperature in the high temperature side separation region is preferably 30°C or higher, particularly preferably 40°C or higher. Phase separation during the operation of the refrigerator considerably adversely affects the service life and the operation efficiency of the apparatus. For example, if phase separation between the refrigerant and lubricating oil occurs in the compressor section, lubricity in a moving member will become insufficient so that seizing and other problems will occur to considerably reduce the service life of the apparatus. On the other hand, if phase separation occurs in the evaporator, the heat exchange efficiency is considerably reduced because of the presence of a highly viscous lubricating oil.

[0003]

As a refrigerant for refrigerators, a chlorofluorocarbon (CFC), a hydrochlorofluorocarbon (HCFC), etc. have been hitherto mainly used. Because these compounds contain chlorine atoms which cause environmental problems, chlorine-free substitutional refrigerants such as a hydrofluorocarbon (HFC) have been investigated. Thus, hydrofluorocarbons, including 1,1,1,2-tetrafluoroethane, difluoromethane, pentafluoroethane, and

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1,1,1-trifluoroethane have become a focus of attention. For example, 1,1,1,2-tetrafluoroethane is actually used in a car air conditioning system.

Since there is an apprehension that HFC may also have a problem with respect to global warming, a natural refrigerant such as carbon dioxide has become a focus of attention as a substitutional refrigerant. However, because carbon dioxide requires a high pressure, it is impossible to use carbon dioxide in current car air conditioning systems.

As a refrigerant having a low global warming potential and being usable for a current car air conditioning system, there has been found a refrigerant having a specific polar structure in its molecule, such as an unsaturated fluorinated hydrocarbon compound (see, for example, Patent Document 1), a fluorinated ether compound (see, for example, Patent Document 2), a fluorinated alcohol compound or a fluorinated ketone compound.

A lubricating oil for refrigerators using such a refrigerant is required to have excellent compatibility with the refrigerant, good sealing properties, capability of imparting a low coefficient of friction to sliding members and, yet, excellent stability.

[0004]

[Patent Document 1] Japanese Translation of PCT International Application Publication No. 2006-503961

[Patent Document 2] Japanese Translation of PCT International Application Publication No. H07-507342

[Disclosure of the Invention]

[0005]

The present invention relates to a lubricating oil composition for refrigerators which is applicable to such refrigerators that use a refrigerant having a low global warming potential, being usable in current car air conditioner systems, and having a specific structure, such as an unsaturated fluorinated hydrocarbon compound, and which has excellent compatibility with the refrigerant, good sealing properties, capability of imparting a low coefficient of friction to sliding members and, yet, excellent stability; and a compressor using such a lubricating oil composition.

[0006]

The inventors have made an earnest study with a view toward accomplishing the above and, as a result, found that the above can be achieved by using a base oil which comprises a specific polyol ester compound and which has specific properties and by preferably using a specific material in a sliding member of a refrigerator. The present invention has been completed based on the above finding.

Thus, the present invention provides as follows:

[0007]

(1) A lubricating oil composition for refrigerators that use a refrigerant comprising

at least one fluorine-containing organic compound selected from among compounds represented by the following molecular formula (A):

$C_pO_qF_rR_s$ (A)

in which R represents Cl, Br, I, or H; p, q, r, and s are integers of 1 to 6, 0 to 2, 1 to 14, and 0 to 13, respectively, with the proviso that when q is 0, p is 2 to 6, and at least one carbon-carbon unsaturated bond is present in the molecule, or a combination of the fluorine-containing organic compound with a saturated fluorinated hydrocarbon compound,

said lubricating oil composition comprising a base oil comprising as a main component a polyol ester compound obtained from a polyhydric alcohol selected from among pentaerythritol, dipentaerythritol, trimethylolpropane and neopentyl glycol, and a C_4 to C_{20} aliphatic monocarboxylic acid, said polyol ester compound having an acid value of 0.02 mgKOH/g or less and a hydroxyl value of 5 mgKOH/g or less;

(2) The lubricating oil composition for refrigerators as defined in above (1), in which the refrigerant is a C_2 to C_3 unsaturated fluorinated hydrocarbon refrigerant or a combination of a C_1 to C_2 saturated fluorinated hydrocarbon refrigerant with a C_3 unsaturated fluorinated hydrocarbon refrigerant.

(3) The lubricating oil composition for refrigerators as defined in above (1) or (2), in which the base oil has a kinematic viscosity at 100°C of 2 to 50 mm^2/s;

(4) The lubricating oil composition for refrigerators as defined in any one of above (1) to (3), in which the base oil has a molecular weight of at least 300;

(5) The lubricating oil composition for refrigerators as defined in any one of above (1) to (4), in which the base oil has a flash point of at least 200°C;

[0008]

(6) The lubricating oil composition for refrigerators as defined in any one of above (1) to (5), further comprising at least one additive selected from the group consisting of an extreme pressure agent, an oiliness agent, an antioxidant, an acid scavenger, and an anti-foaming agent;

(7) The lubricating oil composition for refrigerators as defined in any one of above (1) to (6), in which the refrigerators have a sliding member made of an engineering plastic or having an organic coating film or an inorganic coating film;

(8) The lubricating oil composition for refrigerators as defined in above (7), in which the organic coating film is a polytetrafluoroethylene coating film, a polyimide coating film, a polyamide-imide coating film, or a thermosetting insulating film formed from a resin coating material comprising a resin base material comprising a polyhydroxyether resin and a polysulfone-based resin, and a cross-linking agent;

(9) The lubricating oil composition for refrigerators as defined in above (7), in which the inorganic coating film is a graphite film, a diamond-like carbon film, a tin film, a chromium film, a nickel film, or a molybdenum film;

(10) The lubricating oil composition for refrigerators as defined in any one of above (1) to (9), for use in various hot-water supplying systems or refrigeration and heating systems for car air conditioners, electric car air conditioners, gas heat pumps, air conditioners, refrigerators, vending machines, or showcases;

(11) The lubricating oil composition for refrigerators as defined in above (10), in which a water content and a residual air content within each of the systems are 300 ppm by mass or

[0009]

(12) A compressor using the refrigerator oil composition as defined in above (1);

(13) The compressor as defined in above (12), in which the compressor has a sliding member made of an engineering plastic or having an organic coating film or an inorganic coating film;

(14) The compressor as defined in above (13), in which the engineering plastic is a polyamide resin, a polyphenylene sulfide resin or a polyacetal resin;

(15) The compressor as defined in above (13), in which the organic coating film is a polytetrafluoroethylene coating film, a polyimide coating film, a polyamide-imide coating film, or a thermosetting insulating film formed from a resin coating material comprising a resin base material comprising a polyhydroxyether resin and a polysulfone-based resin, and a cross-linking agent; and

(16) The compressor as defined in above (13), in which the inorganic coating film is a graphite film, a diamond-like carbon film, a tin film, a chromium film, a nickel film, or a molybdenum film.

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[0009a]

More specifically, the present invention provides:

(1) a lubricating oil composition for a refrigerator that uses a refrigerant, comprising: at least one fluorine-containing organic compound represented by the following molecular formula (A): $C_pF_rH_s$ (A) wherein: p, r, and s are integers of 2 to 3, 1 to 6, and 0 to 5, respectively, and wherein at least one carbon-carbon unsaturated bond is present in the molecular formula (A), and said lubricating oil composition comprising a base oil comprising at least 50% by mass of a polyol ester compound obtained from a polyhydric alcohol selected from the group consisting of pentaerythritol, dipentaerythritol, trimethylolpropane and neopentyl glycol, and a C_4 to C_{20} aliphatic monocarboxylic acid, said polyol ester compound having an acid value of 0.02 mgKOH/g or less and a hydroxyl value of 5 mgKOH/g or less;

(2) the lubricating oil composition for refrigerators as defined in item (1), wherein the compound of the molecular formula (A) is a fluorinated propene;

(3) the lubricating oil composition for refrigerators as defined in item (2), wherein the fluorinated propene is at least one selected from various isomers of pentafluoropropene, 3,3,3-trifluoropropene, and 2,3,3,3-tetrafluoropropene;

(4) the lubricating oil composition for refrigerators as defined in any one of items (1) to (3), wherein the base oil has a kinematic viscosity at 100°C of 2 to 50 mm^2/s;

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(5) the lubricating oil composition for refrigerators as defined in any one of items (1) to (4), wherein the base oil has a molecular weight of at least 300 g/mol;

(6) the lubricating oil composition for refrigerators as defined in any one of items (1) to (5), wherein the base oil has a flash point of at least 200°C according to JIS K2265;

(7) the lubricating oil composition for refrigerators as defined in any one of items (1) to (6), further comprising at least one additive selected from the group consisting of an extreme pressure agent, an oiliness agent, an antioxidant, an acid scavenger, and an anti-foaming agent;

(8) the lubricating oil composition for refrigerators as defined in any one of items (1) to (7), wherein the refrigerator has a sliding member made of an engineering plastic or has an organic coating film or an inorganic coating film;

(9) the lubricating oil composition for refrigerators as defined in item (8), wherein the organic coating film is a polytetrafluoroethylene coating film, a polyimide coating film, a polyamide-imide coating film, or a thermosetting insulating film formed from a resin coating material comprising a resin base material comprising a polyhydroxyether resin and a polysulfone-based resin, and a cross-linking agent;

(10) the lubricating oil composition for refrigerators as defined in item (8), wherein the inorganic coating film is a graphite film, a diamond-like carbon film, a tin film, a chromium film, a nickel film, or a molybdenum film;

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(11) the lubricating oil composition for refrigerators as defined in any one of item (1) to (10), for use in a system wherein the system is a car air conditioner, an electric car air conditioner, a gas heat pump, an air conditioner, a refrigerator, a vending machine, or a showcase;

(12) the lubricating oil composition for refrigerators as defined in item (11), wherein a water content and a residual air content within the system are 300 ppm by mass or less and 10 kPa or less, respectively;

(13) a compressor using the refrigerator oil composition as defined in any one of item (1) to (7);

(14) the compressor as defined in item (13), wherein the compressor has a sliding member made of an engineering plastic, or has an organic coating film or an inorganic coating film;

(15) the compressor as defined in item (14), wherein the engineering plastic is a polyamide resin, a polyphenylene sulfide resin, or a polyacetal resin;

(16) the compressor as defined in item (14), wherein the organic coating film is a polytetrafluoroethylene coating film, a polyimide coating film, a polyamide-imide coating film, or a thermosetting insulating film formed from a resin coating material comprising a resin base material comprising a polyhydroxyether resin and a polysulfone-based resin, and a cross-linking agent;

(17) the compressor as defined in item (14), wherein the inorganic coating film is a graphite film, a diamond-like carbon film, a tin film, a chromium film, a nickel film, or a molybdenum film.

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[Effect of the Invention]

[0010]

According to the present invention, it is possible to provide a lubricating oil composition for refrigerators which is used for refrigerators using a refrigerant having a low global warming potential and specific structure, such as an unsaturated fluorinated hydrocarbon compound, and being particularly usable

in current car air conditioner systems and which has excellent compatibility with the refrigerant, good sealing properties, capability of imparting a low coefficient of friction to sliding members and, yet, excellent stability, and a compressor using the lubricating oil composition.

[Best Mode for Carrying out the Invention]

[0011]

The lubricating oil composition for refrigerators according to the present invention is a composition for refrigerators that use a refrigerant comprising at least one fluorine-containing organic compound selected from among compounds represented by the following molecular formula (A):

$C_pO_qF_rR_s$ (A)

in which R represents Cl, Br, I, or H, p, q, r, and s are integers of 1 to 6, 0 to 2, 1 to 14, and 0 to 13, respectively, with the proviso that when q is 0, p is 2 to 6, and at least one carbon-carbon unsaturated bond is present in the molecule, or a combination of the fluorine-containing organic compound with a saturated fluorinated hydrocarbon compound.

[0012]

<Refrigerant>

The above molecular formula (A) shows the kind and the number of each element in the molecule. Thus, represented by the above molecular formula (A) is a fluorine-containing organic compound having a number p of carbon atoms of 1 to 6. Such a C_1 to C_6 fluorine-containing organic compound can show physical and chemical properties required as a refrigerant, such as a boiling point, a freezing point, and a latent heat of evaporation.

In the above molecular formula (A), examples of the bond of the p-number of carbon atoms shown by C_p may include carbon-carbon single bonds, unsaturated bonds such as carbon-carbon double bonds, and carbon-oxygen double bonds. The carbon-carbon unsaturated bond is preferably a carbon-carbon double bond for reasons of stability. The number of the carbon-carbon unsaturated bond is at least one and is preferably one.

In the above molecular formula (A), preferred examples of the bond of the q-number of oxygen atoms shown by O_q may include those derived from ether groups, hydroxyl groups, and carbonyl groups. The number q of the oxygen atom may be two. Thus, molecules having two ether groups, hydroxyl groups, etc. are included in the above molecule.

When q of O_q is zero, namely when no oxygen is contained in the molecule, p should be 2 to 6. The molecule should contain at least one unsaturated bond such as a carbon-carbon double bond. Namely, at least one of the bonds of the p-number of carbon atoms represented by C_p must be a carbon-carbon unsaturated bond.

In the above molecular formula (A), R represents Cl, Br, I, or H and may be any one of them. For reasons of less tendency to destroy the ozone layer, R is preferably H.

Illustrative of suitable fluorine-containing organic compounds represented by the above molecular formula (A) are unsaturated fluorinated hydrocarbons, fluorinated ether compounds, fluorinated alcohol compounds, and fluorinated ketone compounds as described previously.

These compounds will be described below.

[0013]

Unsaturated fluorinated hydrocarbon compound:

As the unsaturated fluorinated hydrocarbon compound used in the present invention as a refrigerant of refrigerators, there may be mentioned, for example, unsaturated fluorinated hydrocarbon compounds of the above molecular formula (A) in which R is H, p is 2 to 6, q is 0, r is 1 to 12, and s is 0 to 11.

Preferred examples of such an unsaturated fluorinated hydrocarbon compound include fluorinated derivatives of C_2 to C_6 straight chained or branched chained olefins and C_4 to C_6 cyclic olefins.

Concrete examples of the unsaturated fluorinated hydrocarbon compound include ethylenes into which 1 to 3 fluorine atoms have been introduced, propenes into which 1 to 5 fluorine atoms have been introduced, butenes into which 1 to 7 fluorine atoms have been introduced, pentenes into which 1 to 9 fluorine atoms have been introduced, hexenes into which 1 to 11 fluorine atoms have been introduced, cyclobutene into which 1 to 5 fluorine atoms have been introduced, cyclopentene into which 1 to 7 fluorine atoms have been introduced, and cyclohexene into which 1 to 9 fluorine atoms have been introduced.

Among the above unsaturated fluorinated hydrocarbon compounds, C_2 to C_3 unsaturated fluorinated hydrocarbon compounds are preferred. More preferred are fluorinated propenes. As the fluorinated propenes, there may be mentioned various isomers of pentafluoropropene, 3,3,3-trifluoropropene, and 2,3,3,3-tetrafluoropropene. Particularly preferred are 1,2,3,3,3-pentafluoropropene and 2,3,3,3-tetrafluoropropene.

In the present invention, the unsaturated fluorinated

hydrocarbon compounds may be used singly or in combination of two or more thereof.

Also suitably used is a combination of a C_1 to C_2 saturated fluorinated hydrocarbon refrigerant with a C_3 unsaturated fluorinated hydrocarbon refrigerant. Examples of such a combination include a combination of the above-mentioned 1,2,3,3,3-pentafluoropropene with CH_2F_2, a combination of 1,2,3,3,3-pentafluoropropene with CHF_2CH_3, and a combination of the above-mentioned 2,3,3,3-tetrafluoropropene with CF_3I.

[0014]

Fluorinated ether compound:

As the fluorinated ether compound used in the present invention as a refrigerant for refrigerators, there may be mentioned, for example, fluorinated ether compounds of the above molecular formula (A) in which R is H, p is 2 to 6, q is 1 to 2, r is 1 to 14, and s is 0 to 13.

Preferred examples of such a fluorinated ether compound include fluorinated derivatives of C_2 to C_6 aliphatic ethers having 1 to 2 ether bonds and straight chained or branched alkyl groups, and fluorinated derivatives of C_3 to C_6 cyclic aliphatic ethers having 1 to 2 ether bonds.

Concrete examples of the fluorinated ether compound include dimethyl ethers into which 1 to 6 fluorine atoms have been introduced, methyl ethyl ethers into which 1 to 8 fluorine atoms have been introduced, dimethoxyethanes into which 1 to 8 fluorine atoms have been introduced, methyl propyl ethers into which 1 to 10 fluorine atoms have been introduced, methyl butyl ethers into which 1 to 12 fluorine atoms have been introduced, ethyl propyl ethers into which 1 to 12 fluorine atoms have been

introduced, oxetanes into which 1 to 6 fluorine atoms have been introduced, 1,3-dioxolans into which 1 to 6 fluorine atoms have been introduced, and tetrahydrofurans into which 1 to 8 fluorine atoms have been introduced.

[0015]

Specific examples of the fluorinated ether compound include hexafluorodimethyl ether, pentafluorodimethyl ether, bis(difluoromethyl) ether, fluoromethyl trifluoromethyl ether, trifluoromethyl methyl ether, perfluorodimethoxymethane, 1-trifluoromethoxy-1,1,2,2-tetrafluoroethane, difluoromethyoxypentafluoroethane, 1-trifluoromethoxy-1,2,2,2-tetrafluoroethane, 1-difluoromethoxy-1,1,2,2-tetrafluoroethane, 1-difluoromethoxy-1,2,2,2-tetrafluoroethane,1-trifluoromethoxy-2,2,2-trifluoroethane, 1-difluoromethoxy-2,2,2-trifluoroethane, perfluorooxetane, perfluoro-1,3-dioxolan, various isomers of pentafluorooxetane, and various isomers of tetrafluorooxetane.

In the present invention, the fluorinated ether compounds may be used singly or in combination of two or more thereof.

[0016]

Fluorinated alcohol compound:

As the fluorinated alcohol compound represented by the molecular formula (A) and used in the present invention as a refrigerant for refrigerators, there may be mentioned, for example, fluorinated ether compounds of the above molecular formula (A) in which R is H, p is 1 to 6, q is 1 to 2, r is 1 to 13, and s is 1 to 13.

Preferred examples of such a fluorinated alcohol compound include fluorinated derivatives of C_1 to C_6 straight chained or branched aliphatic alcohols having 1 to 2 hydroxyl groups.

Concrete examples of the fluorinated alcohol compound include methyl alcohols into which 1 to 3 fluorine atoms have been introduced, ethyl alcohols into which 1 to 5 fluorine atoms have been introduced, propyl alcohols into which 1 to 7 fluorine atoms have been introduced, butyl alcohols into which 1 to 9 fluorine atoms have been introduced, pentyl alcohols into which 1 to 11 fluorine atoms have been introduced, ethyl glycols into which 1 to 4 fluorine atoms have been introduced, and propylene glycols into which 1 to 6 fluorine atoms have been introduced.

[0017]

Specific examples of the fluorinated alcohol compound include monofluoromethyl alcohol, difluoromethyl alcohol, trifluoromethyl alcohol, various isomers of difluoroethyl alcohol, various isomers of trifluoroethyl alcohol, various isomers of tetrafluoroethyl alcohol, pentafluoroethyl alcohol, various isomers of difluoropropyl alcohol, various isomers of trifluoropropyl alcohol, various isomers of tetrafluoropropyl alcohol, various isomers of pentafluoropropyl alcohol, various isomers of hexafluoropropyl alcohol, heptafluoropropyl alcohol, various isomers of difluorobutyl alcohol, various isomers of trifluorobutyl alcohol, various isomers of tetrafluorobutyl alcohol, various isomers of pentafluorobutyl alcohol, various isomers of hexafluorobutyl alcohol, various isomers of hepafluorobutyl alcohol, various isomers of octafluorobutyl alcohol, nonafluorobutyl alcohol, various isomers of difluoroethylene glycol, trifluoroethylene glycol, tetrafluoroethylene glycol, various isomers of difluoropropylene glycol, various isomers of trifluoropropylene glycol, various isomers of tetrafluoropropylene glycol, various isomers of

pentafluoropropylene glycol, fluorinated propylene glycols such as hexafluoropropylene glycol, and fluorinated trimethylene glycols corresponding to the above fluorinated propylene glycols.

In the present invention, the fluorinated alcohol compounds may be used singly or in combination of two or more thereof.

[0018]

Fluorinated ketone compound:

As the fluorinated ketone compound used in the present invention as a refrigerant for refrigerators, there may be mentioned, for example, fluorinated ketone compounds of the above molecular formula (A) in which R is H, p is 2 to 6, q is 1 to 2, r is 1 to 12, and s is 0 to 11.

Preferred examples of such a fluorinated ketone compound include fluorinated derivatives of C_3 to C_6 aliphatic ketones having straight chained or branched alkyl groups.

Concrete examples of the fluorinated ketone compound include acetones into which 1 to 6 fluorine atoms have been introduced, methyl ethyl ketones into which 1 to 8 fluorine atoms have been introduced, diethyl ketones into which 1 to 10 fluorine atoms have been introduced, and methyl propyl ketones into which 1 to 10 fluorine atoms have been introduced.

[0019]

Specific examples of the fluorinated ketone compound include hexafluorodimethyl ketone, pentafluorodimethyl ketone, bis(difluoromethyl) ketone, fluoromethyl trifluoromethyl ketone, trifluoromethyl methyl ketone, perfluoromethyl ethyl ketone, trifluoromethyl-1,1,2,2-tetrafluoroethyl ketone, difluoromethyl pentafluoroethyl ketone, trifluoromethyl-1,1,2,2-

tetrafluoroethyl ketone, difluoromethyl-1,1,2,2-tetrafluoroethyl ketone, difluoromethyl-1,2,2,2-trifluoroethyl ketone, trifluoromethyl-2,2,2-trifluoroethyl ketone, and difluoromethyl-2,2,2-trifluoroethyl ketone.

In the present invention, the fluorinated ketone compounds may be used singly or in combination of two or more thereof.

[0020]

Saturated fluorinated hydrocarbon compound:

The saturated fluorinated hydrocarbon compound is a refrigerant that may be mixed, if necessary, with at least one fluorine-containing organic compound selected from among the compounds represented by the above molecular formula (A).

As the saturated fluorinated hydrocarbon compound, fluorinated derivatives of C_1 to C_4 alkanes may be suitably used. Particularly preferred saturated fluorinated hydrocarbon compounds are fluorinated derivatives of C_1 to C_2 alkanes, e.g. methane and ethane, such as trifluoromethane, difluoromethane, 1,1-difluoroethane, 1,1,1-trifluoroethane, 1,1,2-trifluoroethane, 1,1,1,2-tetrafluoroethane, 1,1,2,2-tetrafluoroethane, and 1,1,1,2,2-pentafluoroethane. The saturated fluorinated hydrocarbon compounds may also be those obtained by halogenating the above fluorinated alkanes with halogen atoms other than fluorine, such as trifluoroiodomethane (CF_3I). The saturated fluorinated hydrocarbon compounds may be used singly or in combination of two or more thereof.

The compounding amount of the saturated fluorinated hydrocarbon compound is generally 30% by mass or less, preferably 20% by mass or less, more preferably 10% by mass or less, based on the total amount of the refrigerant.

[0021]

The lubricating oil composition for refrigerators according to the present invention (hereinafter occasionally referred to as "refrigerator oil composition") is a lubricating oil composition for refrigerators that use the above-described refrigerant and comprises the following base oil.

<Base oil>

As the base oil for the refrigerator oil composition of the present invention, a polyol ester compound prepared from a polyhydric alcohol selected from among pentaerythritol, dipentaerythritol, trimethylolpropane and neopentyl glycol, and a C_4 to C_{20} aliphatic monocarboxylic acid. Among the C_4 to C_{20} aliphatic monocarboxylic acids, preferably used are those which have at least 5 carbon atoms, more preferably at least 6 carbon atoms, particularly preferably at least 8 carbon atoms, from the viewpoint of lubricity. From the viewpoint of compatibility with the refrigerant, preferably used are those which have not more than 18 carbon atoms, more preferably not more than 12 carbon atoms, particularly preferably not more than 9 carbon atoms.

The aliphatic monocarboxylic acid may be straight chained or branched. From the viewpoint of lubricity, straight chained aliphatic monocarboxylic acid is preferred. From the viewpoint of stability against hydrolysis, branched aliphatic monocarboxylic acid is preferred.

Further, both saturated aliphatic monocarboxylic acid and unsaturated aliphatic monocarboxylic acid may be used.

[0022]

As the aliphatic monocarboxylic acid, there may be

mentioned straight chained or branched aliphatic monocarboxylic acids such as pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, decanoic acid, undecanoic acid, dodecanoic acid, tridacanoic acid, tetradecanoic acid, pentadecanoic acid, hexadecanoic acid, heptadecanoic acid, octadecanoic acid, nonadecanoic acid, icosanoic acid and oleic acid, and so called neo acids having a quaternary α-carbon atom. More specifically, illustrative of suitable aliphatic monocarboxylic acid are valeric acid (n-pentanoic acid), caproic acid (n-hexanoic acid), enanthic acid (n-heptanoic acid), caprylic acid (n-octanoic acid), pelargonic acid (n-nonanoic acid), capric acid (n-decanoic acid), oleic acid (cis-9-octadecenoic acid), isopentanoic acid (3-methylbutanoic acid), 2-methylhexanoic acid, 2-ethylpentanoic acid, 2-ethylhexanoic acid, and 3,5,5-trimethylhexanoic acid.

The polyol ester compound may be a partial ester in which not all hydroxyl groups are esterified, a complete ester in which all hydroxyl groups are esterified, or a mixture of the partial ester and the complete ester. The complete ester is preferred, however.

When the ester of a polyhydric alcohol selected from among pentaerythritol, dipentaerythritol, trimethylolpropane, and neopentyl glycol with the above-described aliphatic monocarboxylic acid is a di- or higher ester, such an ester may be obtained from a mixture of aliphatic monocarboxylic acids and the polyhydric alcohol. Such an ester has excellent low temperature properties and compatibility with the refrigerant.

[0023]

The base oil used in the refrigerator oil composition of

the present invention comprises at least one kind of the above-described polyol ester compounds as a main component. As used herein, the term "comprises as a main component" is intended to mean that the polyol ester compound is contained in an amount of at least 50% by mass. The content of the polyol ester compound in the base oil is preferably at least 70% by mass, more preferably at least 90% by mass, still more preferably 100% by mass.

The base oil used in the present invention is particularly suited for the above-described unsaturated fluorinated hydrocarbon refrigerant. Because the refrigerant, which comprises an olefinic structure, has poor stability, the base oil should have an acid value of 0.02 mgKOH/g or less and a hydroxyl value of 5 mgKOH/g or less. The acid value is preferably 0.01 mgKOH/g or less, while the hydroxyl value is preferably 3 mgKOH/g or less.

It is also preferred that the base oil have an ASTM color of 1 or less, a surface tension of 20 mN/m or more, a pH of extracted water of 5.5 or more, an ash content of 0.1% by mass or less, and a volume resistivity of 10^9 Ωm or more. The base oil having the above properties is suited because of its good stability and excellent electric insulation performance.

In preparing the polyol ester compounds, coloration thereof may be suppressed by conducting the esterifying reaction in an inert gas atmosphere. In the reaction between a polyhydric alcohol and an aliphatic monocarboxylic acid, when the amount of the aliphatic monocarboxylic acid is less than the stoichiometric amount, part of the hydroxyl groups remains unreacted so that the hydroxyl value increases. When the amount

of the aliphatic monocarboxylic acid is greater than the stoichiometric amount, on the other hand, part of the carboxylic acids remains unreacted so that the acid value increases and the pH of extracted water deceases. Accordingly, the molar ratio of the polyhydric alcohol to the aliphatic monocarboxylic acid is desired to be controlled in an optimum manner. It is further preferred that a treatment be carried out to reduce the residual amount of the esterifying catalyst (ash) as much as possible.

[0024]

The kinematic viscosity at 100°C of the base oil used in the present invention is preferably 2 to 50 mm^2/s, more preferably 3 to 40 mm^2/s, still more preferably 4 to 30 mm^2/s. A kinematic viscosity of 2 mm^2/s or more can achieve suitable lubricating performance (load carrying property) as well as good sealing property. A kinematic viscosity of 50 mm^2/s or less can provide good energy saving property.

It is preferred that the base oil have a molecular weight of 300 or more, more preferably 500 to 3,000, still more preferably 600 to 2,500. The base oil preferably has a flash point of at least 200°C. When the molecular weight of the base oil is 300 or more, desired performance as a refrigerator oil can be obtained and, at the same time, a flash point of at least 200°C may be achieved. From the standpoint of stability against oxidation, the base oil preferably has an amount of evaporation of 5% by mass or less. The amount of evaporation herein is as measured according to heat stability test (JIS K 2540).

[0025]

In the present invention, the base oil may contain other base oil components in addition to the polyol ester compound in

an amount of not more than 50% by mass, preferably not more than 30% by mass, more preferably not more than 10% by mass, as long as the above properties are ensured. It is still more preferred that the "other base oil components" be not contained.

As the base oil usable together with the polyol ester compound, there may be mentioned, for example, polyoxyalkylene glycols, polyvinyl ethers, copolymers of a poly(oxy)alkylene glycol or its monoether with a polyvinyl ether, other polyesters, polycarbonates, hydrogenated α-olefin oligomers, mineral oils, alicyclic hydrocarbon compounds, and alkylated aromatic hydrocarbon compounds.

The refrigerator oil composition of the present invention may contain at least one additive selected from among an extreme pressure agent, an oiliness agent, an antioxidant, an acid scavenger, and an anti-foaming agent.

As the extreme pressure agent, there may be mentioned phosphorus-based extreme pressure agents such as phosphoric acid esters, acid phosphoric acid esters, phosphorous acid esters, acid phosphorous acid esters, and amine salts of them.

Among these phosphorus-based extreme pressure agents, tricresyl phosphate, trithiophenyl phosphate, tri(nonylphenyl) phosphite, dioleyl hydrogen phosphite, and 2-ethylhexyl diphenyl phosphite are particularly preferred from the viewpoint of extreme pressure property and frictional characteristics.

[0026]

As the extreme pressure agent, there may also be mentioned carboxylic acid metal salts. The "carboxylic acid metal salt" as used herein is a metal salt of carboxylic acids having preferably 3 to 60 carbon atoms, more preferably 3 to 30 carbon

atoms, particularly preferably a metal salt of fatty acids having 12 to 30 carbon atoms. There may also be mentioned metal salts of dimer acids and trimer acids of the above-described fatty acids and metal salts of dicarboxylic acids having 3 to 30 carbon atoms. Above all, metal salts of C_{12} to C_{30} fatty acids and C_3 to C_{30} dicarboxylic acids are particularly preferred.

As the metal constituting the above metal salts, alkali metals and alkaline earth metals are preferred. Particularly preferred are alkali metals.

As extreme pressure agents other than those described above, there may also be mentioned, for example, sulfur-based extreme pressure agents such as sulfurized fats and oils, sulfurized fatty acids, sulfurized esters, sulfurized olefins, dihydrocarbyl polysulfides, thiocarbamates, thioterpenes, and dialkyl thiodipropionates.

The compounding amount of the extreme pressure agent is generally 0.001 to 5% by mass, preferably 0.005 to 3% by mass, based on the total amount of the composition from the standpoint of lubricity and stability.

In the present invention, the above-described extreme pressure agents may be used singly or in combination with two or more thereof.

[0027]

Examples the oiliness agent include saturated or unsaturated aliphatic monocarboxylic acids such as stearic acid and oleic acid, polymerized fatty acids such as dimer acids and hydrogenated dimer acids, hydroxy fatty acids such as ricinoleic acid and 12-hydroxystearic acid, saturated or unsaturated aliphatic monoalcohols such as lauryl alcohol and oleyl alcohol,

saturated or unsaturated aliphatic monoamines such as stearyl amine and oleyl amine, saturated or unsaturated aliphatic monocarboxylic acid amides such as lauramide and oleamide, and partial esters of polyhydric alcohols such as glycerol and sorbitol with saturated or unsaturated aliphatic monocarboxylic acids.

These oiliness agents may be used singly or in combination of two or more thereof. The compounding amount of the oiliness agent is generally in the range of 0.01 to 10% by mass, preferably 0.1 to 5% by mass, based on the total amount of the composition.

[0028]

As the antioxidant, there may be preferably used phenol-based antioxidants such as 2,6-di-tert-butyl-4-methylphenol, 2,6-di-tert-butyl-4-ethylphenol, and 2,2'-methylenebis(4-methyl-6-tert-butylphenol) and amine-based antioxidants such as phenyl-α-naphthylamine and N,N'-diphenyl-p-phenylenediamine. The compounding amount of the antioxidant is generally 0.01 to 5% by mass, preferably 0.05 to 3% by mass, based on the total amount of the composition from the standpoint of the anti-oxidizing effect and economy.

[0029]

As the acid scavenger, there may be mentioned epoxy compounds such as, for example, phenyl glycidyl ether, alkyl glycidyl ethers, alkylene glycol glycidyl ethers, phenyl glycidyl ester, alkyl glycidyl esters, alkenyl glycidyl esters, cyclohexene oxide, α-olefin oxides, and epoxidized soybean oil. Above all, phenyl glycidyl ethers, alkyl glycidyl ethers, alkylene glycidyl ethers, glycidyl-2,2-dimethyl octanoate,

glycidyl benzoate, glycidyl-tert-butyl benzoate, glycidyl acrylate, glycidyl methacrylate, cyclohexene oxide, and α-olefin oxides are preferred for reasons of compatibility.

The alkyl group of the alkyl glycidyl ethers and the alkylene group of the alkylene glycol glycidyl ethers may be branched and have generally 3 to 30, preferably 4 to 24, particularly preferably 6 to 16 carbon atoms. The α-olefin oxides having a total carbon atoms of 4 to 50, preferably 4 to 24, particularly preferably 6 to 16 carbon atoms are generally used. In the present invention, the acid scavengers may be used singly or in combination of two or more thereof. The compounding amount of the acid scavenger is generally in the range of 0.005 to 5% by mass, preferably 0.05 to 3% by mass, based on the total amount of the composition from the standpoint of the scavenging effect and suppression of sludge formation.

[0030]

In the present invention, the stability of the refrigerator oil composition may be improved by compounding the acid scavenger thereinto. The stability may be further improved by using the above described extreme pressure agent and antioxidant together with the acid scavenger.

As the anti-foaming agent, there may be mentioned silicone oil and fluorinated silicone oil.

The refrigerator oil composition of the present invention may be further compounded with various other known additives such as copper deactivator, e.g. N-[N,N'-dialkyl(C_3 to C_{12} alkyl)aminomethyl]triazole, as long as the objects of the present invention are not adversely affected.

[0031]

The refrigerator oil composition of the present invention may be suitably applied to such refrigerators that use a refrigerant comprising at least one fluorine-containing organic compound selected from among compounds represented by the above molecular formula (A) or a combination of the fluorine-containing organic compound with a saturated fluorinated hydrocarbon compound, and is particularly suited for use in refrigerators that use a refrigerant comprising an unsaturated fluorinated hydrocarbon compound.

In the method of lubricating the refrigerators using the refrigerator oil composition of the present invention, the using amount of the above-described various refrigerants and the refrigerator oil composition is preferably such that a mass ratio of the refrigerant to the refrigerator oil composition is in the range of 99:1 to 10:90, more preferably 95:5 to 30:70. When the amount of the refrigerant is less than the above-specified range, the refrigerating performance tends to be deteriorated. When the amount of the refrigerant is greater than the above-specified range, the lubricating performance tends to be undesirably deteriorated. The refrigerator oil composition of the present invention may be applied to various refrigerators and may be particularly suitably used in a compression refrigerating cycle of compression-type refrigerators.

[0032]

The refrigerators to which the refrigerator oil composition of the present invention is applied has a refrigerating cycle comprising, as its essential components, a combination of a compressor, a condenser, an expansion system

(such as expansion valve), and an evaporator, or a combination of a compressor, a condenser, an expansion system, a dryer, and an evaporator. These refrigerators use the refrigerator oil composition of the present invention as a refrigerating machine oil and various refrigerants as described above.

The dryer is preferably filled with a drying agent including zeolite having a pore diameter of 0.33 nm or less. Examples of the zeolite include natural zeolite and synthetic zeolite. Particularly suitably used is zeolite having a CO_2 gas absorption capacity of 1.0% or less at 25°C under a CO_2 gas partial pressure of 33 kPa. Specific examples of the synthetic zeolite having such an absorption capacity include those available under trade names XH-9 and XH-600 from Union Showa Co., Ltd.

When such a drying agent is used in the present invention, water may be efficiently removed from the refrigerating cycle without absorbing the refrigerant present in the refrigerating cycle. At the same time, such a drying agent itself is prevented from being deteriorated and powdered. Thus, occurrence of clogging of pipes with the powder and abnormal wear due to intrusion of the powder into sliding members of the compressors can be avoided. Therefore, the refrigerators can be operated in a stable manner for a long period of time.

[0033]

In the refrigerators to which the refrigerator oil composition of the present invention is applied, various sliding members (for example, bearings) are provided within the compressor thereof. In the present invention, these sliding members are preferably made of an engineering plastic or

provided with an organic coating film or an inorganic coating film from the standpoint of sealing property, in particular.

As the preferred engineering plastic, there may be mentioned, for example, a polyamide resin, a polyphenylene sulfide resin, and a polyacetal resin from the standpoint of sealing property, sliding property, and abrasion resistance.

As the preferred organic coating film, there may be mentioned, for example, a fluorine-containing resin coating film (such as a polytetrafluoroethylene coating film), a polyimide coating film, a polyamide-imide coating film, and a thermosetting insulating film formed from a resin coating material comprising a resin base material comprising a polyhydroxyether resin and a polysulfone-based resin and a cross-linking agent from the standpoint of sealing property, sliding property, and abrasion resistance.

As the preferred inorganic coating film, there may be mentioned, for example, a graphite film, a diamond-like carbon film, a nickel film, a molybdenum film, a tin film, and a chromium film from the standpoint of sealing property, sliding property, and abrasion resistance. These inorganic coating films may be formed by a plating method or by a PVD (physical vapor deposition) method.

If desired, the sliding members may be made of a conventional alloy such as a Fe-based alloy, an Al-based alloy, and a Cu-based alloy.

[0034]

The refrigerator oil composition of the present invention may be suitably used in various hot-water supplying systems or refrigeration and heating systems for car air conditioners,

electric car air conditioners, gas heat pumps, air conditioners, refrigerators, vending machines, or showcases.

In the present invention, the water content in these systems is preferably 300 ppm by mass or less, more preferably 200 ppm by mass or less. The residual air content in the systems is preferably 10 kPa or less, more preferably 5 kPa or less.

The refrigerator oil composition of the present invention comprises a specific oxygen-containing compound as a main component of a base oil and has a low viscosity, an improved energy saving property and, yet, an excellent sealing property.

[0035]

A compressor (a compressor for a refrigerator) of the present invention is one which uses the above-described refrigerator oil composition, namely a compressor using the above-described refrigerator oil composition in conjunction with a refrigerant comprising at least one fluorine-containing organic compound selected from among compounds represented by the molecular formula (A) or a combination of the fluorine-containing organic compound with a saturated fluorinated hydrocarbon compound.

A part or all of the sliding members of the compressor are preferably made of an engineering plastic or have an organic coating film or an inorganic coating film. As the sliding member, there may be mentioned a sliding interface between a swash plate and a shoe, a sliding interface between a shoe and a piston, and a sliding interface between a piston and a cylinder block, in the case of a swash plate compressor, for example. When at least a part of such sliding members is made of an

engineering plastic or has an organic coating film or an inorganic coating film, the sealing property of a compressor or a refrigerator having the compressor may be improved. Additionally, the sliding property and wear resistance may be also improved.

Preferred examples of the engineering plastic, organic coating film, and inorganic coating film are as described previously.

[Examples]

[0036]

The present invention will be next described in more detail by way of examples. The scope of the present invention is, however, not limited to these examples in any way.

The properties of the base oil and various characteristics of the refrigerator oil composition of the present invention are determined in the manner described below.

Properties of base oil:

(1) Kinematic viscosity at 100°C

The kinematic viscosity was measured using a glass capillary viscometer according to JIS K2283-1983.

(2) Flash Point

The flash point was measured by C.O.C. method according to JIS K2265.

(3) Molecular weight

The molecular weight is a value calculated on the basis of the chemical structure of each compound constituting the base oil.

(4) Acid value

The acid value was measured in accordance with JIS K 2501.

(5) Hydroxyl value

The hydroxyl value was measured in accordance with JIS K 0070.

Characteristics of refrigerator oil composition:

(6) Two-layer separation temperature

An oil/refrigerant (0.6 g/2.4 g) mixture was charged in a two-layer separation temperature measuring tube (inside volume: 10 mL) and maintained in a thermostatic chamber. The temperature in the thermostatic chamber was increased from room temperature (25°C) at a rate of 1°C/min to determine the temperature at which the mixture was separated into two layers.

The refrigerant used was 1,2,3,3,3-pentafluoropropene ("PC07052" manufactured by Apollo Scientific Limited).

(7) Stability (sealed tube test)

A metal catalyst composed of iron, copper, and aluminum was charged in a glass tube together with an oil/refrigerant (4 mL/1 g) mixture (water content: 200 ppm), and the glass tube was then sealed. This was allowed to stand at 175°C under the atmospheric pressure of 26.6 kPa for 30 days. Thereafter, appearance of the oil, appearance of the catalyst, and sludge formation were determined with naked eyes, and an acid value was measured. The refrigerant was the same as that used in (6) above.

(8) Seizing test

A coated Falex seizing test was carried out under conditions including pin/block of A4032/AISIC1137, revolution number of 1,200 rpm, load of 223N, oil amount of 4 μL, and refrigerant pressure of 1 MPa. The refrigerant was the same as

that used in (6) above.

[0037]

The components used for the preparation of the refrigerator oil composition are shown below. The base oil used are A1 to A23. The compound names and properties of the base oils are shown in Table 1.

[0038]

Table 1

Base Oil	Chemical Name	Acid value (mgKOH/g)	Hydroxyl value (mgKOH/g)	Kinematic Viscosity at 100°C(mm^2)	Flash point (°C)
A1	Pentaerythritol Octanoate nonanoate mixed ester (C_8/C_9 molar ratio: 1/1.1) (Molecular weight: 669)	0.00	3>	9.64	260
A2		0.01	3	9.66	
A3		0.02	3>	9.71	
A4		0.02	4	9.64	
A5		0.05	3>	9.61	
A6		0.10	3>	9.57	-
A7		0.01	8	9.69	
A8		0.01	15	9.73	
A9		0.10	8	9.64	
A10	Pentaerythritol Octanoate nonanoate mixed ester (C_8/C_9 molar ratio: 1/1.7) (Molecular weight: 675)	0.00	3>	15.99	
A11		0.01	3	16.15	
A12		0.05	3>	16.25	-
A13		0.01	8	16.32	
A14		0.05	8	16.05	
A15	Neopentylglycol dioctanoate (Molecular weight: 356)	0.00	3>	3.54	
A16		0.05	3>	3.52	-
A17		0.01	10	3.72	
A18	Trimethylolpropane trinonanoate (Molecular weight: 540)	0.00	3>	6.32	
A19		0.05	3>	6.29	-
A20		0.01	10	6.34	
A21	Dipentaerythritol hexahexanoate (Molecular weight: 842)	0.00	3>	20.25	
A22		0.05	3>	20.78	-
A23		0.01	10	20.03	

[0039]

Remarks:

Octanoic acid: 2-ethylhexanoic acid

Nonanoic acid: 3,3,5-trimethylhexanoic acid

Properties of base oil A1 (except those described in Table 1):

ASTM Color: L0.5

Surface tension: 34.7mN/m

pH of extracted water: 6.4

Ash content: less than 0.1% by mass

Volume resistivity: 10^{11} Ωm

[0040]

As an additive, antioxidant B1 (2,6-di-t-butyl-4-methylphenol) was used.

[0041]

Examples 1 to 9 and Comparative Examples 1 to 14

Refrigerator oil compositions as composed in Table 2 were prepared and evaluated for the characteristics thereof using 1,2,3,3,3-pentafluoropropene as a refrigerant. The results are summarized in Table 2.

[0042]

Table 2-1-1

			Example				
			1	2	3	4	5
Blending composition	Base oil	Kind	A1	A2	A3	A4	A10
		(% by mass)	99.5	99.5	99.5	99.5	99.5
	Additive	Antioxidant	B1	B1	B1	B1	B1
		(% by mass)	0.5	0.5	0.5	0.5	0.5
Performance Evaluation	Two-layer separation temperature (oil: 20%) (°C)		40<	40<	40<	40<	40<
	Sealed Tube test	Oil appearance	good	good	good	good	good
		Catalyst appearance	good	good	good	good	good
		Presence or absence of sludge	absent	absent	absent	absent	absent
		Acid value (mgKOH/g)	0.00	0.01	0.02	0.06	0.01
	Seizing test [seizing time] (sec)		95	90	85	90	90

Table 2-1-2

			Example			
			6	7	8	9
Blending composition	Base oil	Kind	A11	A15	A18	A21
		(% by mass)	99.5	99.5	99.5	99.5
	Additive	Antioxidant	B1	B1	B1	B1
		(% by mass)	0.5	0.5	0.5	0.5
Performance Evaluation	Two-layer separation temperature (oil: 20%) (°C)		40<	40<	40<	40<
	Sealed Tube test	Oil appearance	good	good	good	good
		Catalyst appearance	good	good	good	good
		Presence or absence of sludge	absent	absent	absent	absent
		Acid value (mgKOH/g)	0.01	0.01	0.01	0.01
	Seizing test [seizing time] (sec)		90	90	90	90

[0043]

Table 2-2-1

			Comparative Example			
			1	2	3	4
Blending composition	Base oil	Kind	A5	A6	A7	A8
		(% by mass)	99.5	99.5	99.5	99.5
	Additive	Antioxidant	B1	B1	B1	B1
		(% by mass)	0.5	0.5	0.5	0.5
Performance Evaluation	Two-layer separation temperature (oil: 20%) (°C)		40<	40<	40<	40<
	Sealed Tube test	Oil appearance	yellow	brown	yellow	brown
		Catalyst appearance	FeCu colored	FeCu colored	FeCu colored	FeCu colored
		Presence or absence of sludge	trace	present	trace	present
		Acid value (mgKOH/g)	0.51	1.2	0.17	0.38
	Seizing test [seizing time] (sec)		65	60	55	45

Table 2-2-2

			Comparative Example		
			5	6	7
Blending composition	Base oil	Kind	A9	A12	A13
		(% by mass)	99.5	99.5	99.5
	Additive	Antioxidant	B1	B1	B1
		(% by mass)	0.5	0.5	0.5
Performance Evaluation	Two-layer separation temperature (oil: 20%) (°C)		40<	40<	40<
	Sealed tube test	Oil appearance	brown	yellow	yellow
		Catalyst appearance	FeCu colored	FeCu colored	FeCu colored
		Presence or absence of sludge	present	trace	trace
		Acid value (mgKOH/g)	2.5	0.46	0.15
	Seizing test [seizing time] (sec)		30	75	65

[0044]

Table 2-3-1

			Comparative Example			
			8	9	10	11
Blending composition	Base oil	Kind	A14	A16	A17	A19
		(% by mass)	99.5	99.5	99.5	99.5
	Additive	Antioxidant	B1	B1	B1	B1
		(% by mass)	0.5	0.5	0.5	0.5
Performance Evaluation	Two-layer separation temperature (oil: 20%) (°C)		40<	40<	40<	40<
	Sealed Tube test	Oil appearance	brown	yellow	yellow	yellow
		Catalyst appearance	FeCu colored	FeCu colored	FeCu colored	FeCu colored
		Presence or absence of sludge	trace	trace	trace	trace
		Acid value (mgKOH/g)	1.8	0.38	0.13	0.42
	Seizing test [seizing time] (sec)		40	53	45	60

Table 2-3-2

			Comparative Example		
			12	13	14
Blending composition	Base oil	Kind	A20	A22	A23
		(% by mass)	99.5	99.5	99.5
	Additive	Antioxidant	B1	B1	B1
		(% by mass)	0.5	0.5	0.5
Performance Evaluation	Two-layer separation temperature (oil: 20%) (°C)		40<	40<	40<
	Sealed Tube test	Oil appearance	yellow	yellow	yellow
		Catalyst appearance	FeCu colored	FeCu colored	FeCu colored
		Presence or absence of sludge	trace	trace	trace
		Acid value (mgKOH/g)	0.17	0.64	0.21
	Seizing test [seizing time] (sec)		50	70	60

As will be appreciated from Table 2, the refrigerator oil compositions of the present invention (Examples 1 to 9) have a two-layer separation temperature higher than 40°C with the 1,2,3,3,3-pentafluoropropene refrigerant; show excellent stability in the sealed tube test using the 1,2,3,3,3-pentafluoropropene refrigerant; and have a longer seizing time in the coated Falex seizing test.

[Industrial applicability]

[0045]

The lubricating oil composition for refrigerators according to the present invention is usable for refrigerators using a refrigerant having a specific structure, such as an unsaturated fluorinated hydrocarbon compound, having a low global warming potential and particularly being used in current car air conditioner systems and has excellent compatibility with the refrigerant, good sealing properties, capability of imparting a low coefficient of friction to sliding members and, yet, excellent stability.

73162-227

CLAIMS:

1. A lubricating oil composition for a refrigerator that uses a refrigerant, comprising:

at least one fluorine-containing organic compound represented by the following molecular formula (A):

$C_pF_rH_s$ (A)

wherein:

p, r, and s are integers of 2 to 3, 1 to 6, and 0 to 5, respectively, and

wherein at least one carbon-carbon unsaturated bond is present in the molecular formula (A),

and

said lubricating oil composition comprising a base oil comprising at least 50% by mass of a polyol ester compound obtained from a polyhydric alcohol selected from the group consisting of pentaerythritol, dipentaerythritol, trimethylolpropane and neopentyl glycol, and a C_4 to C_{20} aliphatic monocarboxylic acid, said polyol ester compound having an acid value of 0.02 mgKOH/g or less and a hydroxyl value of 5 mgKOH/g or less.

2. The lubricating oil composition for refrigerators as defined in claim 1, wherein the compound of the molecular formula (A) is a fluorinated propene.

3. The lubricating oil composition for refrigerators as defined in claim 2, wherein the fluorinated propene is at least one selected from various isomers of pentafluoropropene, 3,3,3-trifluoropropene, and 2,3,3,3-tetrafluoropropene.

4. The lubricating oil composition for refrigerators as defined in any one of claims 1 to 3, wherein the base oil has a kinematic viscosity at 100°C of 2 to 50 mm^2/s.

5. The lubricating oil composition for refrigerators as defined in any one of claims 1 to 4, wherein the base oil has a molecular weight of at least 300 g/mol.

6. The lubricating oil composition for refrigerators as defined in any one of claims 1 to 5, wherein the base oil has a flash point of at least 200°C according to JIS K2265.

7. The lubricating oil composition for refrigerators as defined in any one of claims 1 to 6, further comprising at least one additive selected from the group consisting of an extreme pressure agent, an oiliness agent, an antioxidant, an acid scavenger, and an anti-foaming agent.

8. The lubricating oil composition for refrigerators as defined in any one of claims 1 to 7, wherein the refrigerator has a sliding member made of an engineering plastic or has an organic coating film or an inorganic coating film.

9. The lubricating oil composition for refrigerators as defined in claim 8, wherein the organic coating film is a polytetrafluoroethylene coating film, a polyimide coating film, a polyamide-imide coating film, or a thermosetting insulating film formed from a resin coating material comprising a resin

base material comprising a polyhydroxyether resin and a polysulfone-based resin, and a cross-linking agent.

10. The lubricating oil composition for refrigerators as defined in claim 8, wherein the inorganic coating film is a graphite film, a diamond-like carbon film, a tin film, a chromium film, a nickel film, or a molybdenum film.

11. The lubricating oil composition for refrigerators as defined in any one of claims 1 to 10, for use in a system wherein the system is a car air conditioner, an electric car air conditioner, a gas heat pump, an air conditioner, a refrigerator, a vending machine, or a showcase.

12. The lubricating oil composition for refrigerators as defined in claim 11, wherein a water content and a residual air content within the system are 300 ppm by mass or less and 10 kPa or less, respectively.

13. A compressor using the refrigerator oil composition as defined in any one of claims 1 to 7.

14. The compressor as defined in claim 13, wherein the compressor has a sliding member made of an engineering plastic, or has an organic coating film or an inorganic coating film.

15. The compressor as defined in claim 14, wherein the engineering plastic is a polyamide resin, a polyphenylene sulfide resin, or a polyacetal resin.

16. The compressor as defined in claim 14, wherein the organic coating film is a polytetrafluoroethylene coating film, a polyimide coating film, a polyamide-imide coating film, or a thermosetting insulating film formed from a resin coating

material comprising a resin base material comprising a polyhydroxyether resin and a polysulfone-based resin, and a cross-linking agent.

17. The compressor as defined in claim 14, wherein the inorganic coating film is a graphite film, a diamond-like carbon film, a tin film, a chromium film, a nickel film, or a molybdenum film.