

DESCRIPTION

Title of Invention

REFRIGERATOR OIL, WORKING FLUID COMPOSITION FOR
REFRIGERATORS, AND REFRIGERATOR

5 Technical Field

[0001] The present invention relates to a refrigerating machine oil, a working fluid composition for a refrigerating machine, and a refrigerating machine.

Background Art

10 [0002] A refrigerating machine such as a refrigerator includes a refrigerant circulation system including a compressor, a condenser, an expansion mechanism (expansion valve, capillary), an evaporator, and the like, and cooling is performed by circulating a refrigerant in the refrigerant circulation system.

15 [0003] Compressors for refrigerating machines include rotary compressors, piston-crank compressors, and the like. For example, in a piston-crank compressor, a rotary motion of a motor is converted into a reciprocating motion by a connecting rod, and a piston coupled to the connecting rod is reciprocated to compress a refrigerant. The
20 refrigerating machine oil is sealed in the compressor together with a refrigerant, and lubricates sliding members such as a connecting rod and a piston. As the refrigerating machine oil, for example, Patent Document 1 below discloses a refrigerating machine oil containing a predetermined base oil, a phosphorus-based extreme pressure agent, and
25 an ester-based additive.

Citation List

Patent Document

[0004] [Patent Document 1] International Publication No. 2005/012469

Summary of Invention**Technical Problem**

5 [0005] Conventional refrigerating machine oils are effective for reducing friction in, for example, a fluid-lubricated region. However, the effect of reducing friction cannot be sufficiently obtained in a region where sliding speed is low, such as an elastic fluid-lubricated region, a mixed lubricated region, or a boundary-lubricated region, and there is still room
10 for improvement in this respect.

[0006] The present invention has been made in view of the above-described circumstances, and an object thereof is to provide a refrigerating machine oil having excellent friction characteristics in a low sliding speed region, a working fluid composition for a refrigerating
15 machine containing the refrigerating machine oil, and a refrigerating machine filled with the refrigerating machine oil.

Solution to Problem

[0007] The present invention provides a refrigerating machine oil comprising: a lubricating base oil having a kinematic viscosity at 40°C of
20 10 mm²/s or less; and an oiliness agent comprising at least one selected from the group consisting of an ester oiliness agent and an ether oiliness agent.

[0008] The lubricating base oil may comprise a mineral oil.

[0009] The oiliness agent may comprise an ether oiliness agent.

25 [0010] The ether oiliness agent may be an alkyl or alkenyl glyceryl ether.

[0011] The present invention also provides a working fluid composition

for a refrigerating machine comprising: a refrigerant; and the refrigerating machine oil according to the present invention.

[0012] The present invention further provides a refrigerating machine comprising a refrigerant circulation system wherein a compressor, a condenser, an expansion mechanism, and an evaporator are connected by piping in this order, wherein the refrigerant circulation system is filled with a refrigerant and the refrigerating machine oil according to the present invention described above.

Advantageous Effects of Invention

[0013] According to the present invention, it is possible to provide a refrigerating machine oil having excellent friction characteristics in a low sliding speed region, a working fluid composition for a refrigerating machine containing the refrigerating machine oil, and a refrigerating machine filled with the refrigerating machine oil.

Brief Description of Drawings

[0014] FIG. 1 is a schematic diagram illustrating an embodiment of the refrigerating machine.

Description of Embodiments

[0015] Embodiments of the present invention will now be described in detail.

[0016] The refrigerating machine oil according to the present embodiment contains a lubricating base oil having a kinematic viscosity at 40°C of 10 mm²/s or less, and an oiliness agent containing at least one selected from the group consisting of an ester oiliness agent and an ether oiliness agent.

[0017] The lubricating base oil may be any of a mineral oil, a synthetic

oil, or a mixture of both. However, from the viewpoint of exhibiting more excellent friction characteristics in a region where the sliding speed is low, the lubricating base oil preferably contains the mineral oil. When the lubricating base oil contains the mineral oil, the content of the mineral oil may be 50% by mass or more, 70% by mass or more, or 90% by mass or more, based on the total amount of the lubricating base oil.

[0018] Examples of the mineral oil include paraffinic or naphthenic mineral oils obtained by subjecting a lubricating oil fraction obtained by atmospheric distillation and vacuum distillation of crude oil to refining treatment such as solvent deasphalting, solvent extraction, hydrocracking, solvent dewaxing, catalytic dewaxing, hydrotreating, sulfuric acid washing, and clay treatment alone or in an appropriate combination of two or more thereof, and paraffinic mineral oils are particularly suitably used. These mineral oils may be used alone or in combination of two or more thereof at an any ratio.

[0019] The paraffinic mineral oil may have a ratio of $\%C_P$ to $\%C_N$ ($\%C_P/\%C_N$) of preferably greater than 1, more preferably 1.1 or greater, and still more preferably 1.5 or greater. When the $\%C_P/\%C_N$ of the paraffinic mineral oil is greater than 1, it is possible to obtain a refrigerating machine oil having an improved flash point (for example, 100°C or higher) and more excellent friction characteristics. In the present invention, $\%C_P$ and $\%C_N$ mean values measured by a method (n-d-M ring analysis) in accordance with ASTM D3238-95 (2010).

[0020] Examples of the synthetic oil include synthetic hydrocarbon oils and oxygen-containing oils.

[0021] Examples of the synthetic hydrocarbon oil include an

alkylbenzene, an alkylnaphthalene, a poly- α -olefin (PAO), a polybutene, and an ethylene- α -olefin copolymer.

[0022] Examples of the oxygen-containing oil include esters, ethers, carbonates, ketones, silicones, and polysiloxanes. Examples of the ester include monoesters, polyol esters, aromatic esters, dibasic acid esters, complex esters, carbonic acid esters, and mixtures thereof. It is preferable to use a monoester of a monohydric aliphatic alcohol and a monocarboxylic fatty acid, and it is desirable to use a mixture of the monoester and a polyol ester of a di- to hexa-hydric alcohol and a monocarboxylic fatty acid as necessary. Examples of the monohydric aliphatic alcohol constituting the ester include monohydric aliphatic alcohols having 1 to 20 carbon atoms, preferably 4 to 18 carbon atoms, and more preferably 4 to 12 carbon atoms. Examples of the monocarboxylic fatty acid constituting the esters include monocarboxylic fatty acids having 1 to 20 carbon atoms, preferably 4 to 18 carbon atoms, and more preferably 4 to 12 carbon atoms. The di- to hexa-hydric alcohol constituting the ester is preferably neopentyl glycol, trimethylolpropane, pentaerythritol, dipentaerythritol, or the like. Examples of the ether include polyvinyl ether, polyalkylene glycol, polyphenyl ether, perfluoroether, and mixtures thereof.

[0023] The kinematic viscosity at 40°C of the lubricating base oil needs to be 10 mm²/s or less, preferably 5 mm²/s or less, and more preferably 4 mm²/s or less, from the viewpoint of effectively reducing the friction coefficient in a region where the sliding speed is low. The lower limit of the kinematic viscosity at 40°C of the lubricating base oil is not particularly limited, and may be, for example, 1 mm²/s or more, or 1.5

mm²/s or more. The lubricating base oil may have a kinematic viscosity at 100°C of preferably 0.5 mm²/s or more, more preferably 1 mm²/s or more. The lubricating base oil may have a kinematic viscosity at 100°C of preferably 3 mm²/s or less, more preferably 2 mm²/s or less. The
5 kinematic viscosity in the present invention means a kinematic viscosity measured in accordance with JIS K2283:2000.

[0024] The flash point of the lubricating base oil may be, for example, 100°C or more, 110°C or more, or 120°C or more, from the viewpoint of safety. The flash point of the lubricating base oil may be, for example,
10 155°C or less, or 145°C or less. The flash point in the present invention means a flash point measured in accordance with JIS K2265-4:2007 (Cleveland Release (COC) method).

[0025] The pour point of the lubricating base oil may be preferably -10°C or less, more preferably -20°C or less. The pour point in the present
15 invention means a pour point measured in accordance with JIS K2269:1987.

[0026] The content of the lubricating base oil may be 50% by mass or more, 60% by mass or more, 70% by mass or more, 80% by mass or more, or 90% by mass or more, based on the total amount of the
20 refrigerating machine oil.

[0027] The refrigerating machine oil according to the present embodiment contains an oiliness agent containing at least one selected from the group consisting of an ester oiliness agent and an ether oiliness agent.

25 [0028] The ester oiliness agent may be a natural product (usually contained in natural oils and fats derived from animals and plants or the

like) or a synthetic product, but is preferably a synthetic ester from the viewpoint of stability of the obtained refrigerating machine oil, uniformity of the ester component, and the like.

5 [0029] Synthetic esters as the ester oiliness agent are obtained, for example, by reacting an alcohol with a carboxylic acid. The alcohol may be a monohydric alcohol or a polyhydric alcohol. The carboxylic acid may be a monobasic acid or a polybasic acid.

10 [0030] The combination of the alcohol and the carboxylic acid of the ester oiliness agent is any combination and is not particularly limited, and examples thereof include esters according to the following combinations (i) to (vii):

- (i) an ester of a monohydric alcohol and a monobasic acid;
- (ii) an ester of a polyhydric alcohol and a monobasic acid;
- (iii) an ester of a polyhydric alcohol and a polybasic acid;
- 15 (iv) an ester of a polyhydric alcohol and a polybasic acid;
- (v) a mixed ester of a mixture of a monohydric alcohol and a polyhydric alcohol and a polybasic acid;
- (vi) a mixed ester of a polyhydric alcohol and a mixture of a monobasic acid and a polybasic acid; and
- 20 (vii) a mixed ester of a mixture of a monohydric alcohol and a polyhydric alcohol and a mixture of a monobasic acid and a polybasic acid.

25 [0031] The esters (ii) to (vii) may be complete esters in which all of the hydroxyl groups of the polyhydric alcohol or the carboxyl groups of the polybasic acid are esterified, or may be partial esters in which some of the hydroxyl groups or the carboxyl groups remain as hydroxyl groups or carboxyl groups.

[0032] As the monohydric alcohol constituting the ester oiliness agent, an alcohol having usually 1 to 24 carbon atoms, preferably 1 to 12 carbon atoms, and more preferably 1 to 8 carbon atoms is used. Such an alcohol may be linear or branched, and may be saturated or unsaturated.

5 Preferred examples of the monohydric alcohol include methanol, ethanol, propanol, butanol, pentanol, hexanol, heptanol, octanol, nonanol, decanol, undecanol, dodecanol, tridecanol, tetradecanol, pentadecanol, hexadecanol, heptadecanol, octadecanol, and mixtures thereof.

[0033] As the polyhydric alcohol constituting the ester oiliness agent, a di- to deca-hydric alcohol is usually used, and di- to hexa-hydric alcohol is preferably used. Preferred examples of the polyhydric alcohol include glycerin, sorbitol, sorbitan, ethylene glycol, propylene glycol, neopentyl glycol, trimethylolethane, trimethylolpropane, pentaerythritol, and mixtures thereof.

15 [0034] As the monobasic acid constituting the ester oiliness agent, a fatty acid having 2 to 24 carbon atoms is usually used. The fatty acid may be linear or branched, and may be saturated or unsaturated. Preferred examples of the monobasic acid include acetic acid, propionic acid, butanoic acid, pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, decanoic acid, undecanoic acid, dodecanoic acid, tridecanoic acid, tetradecanoic acid, pentadecanoic acid, hexadecanoic acid, heptadecanoic acid, octadecanoic acid, octadecenoic acid, lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid, linoleic acid, and linolenic acid.

25 [0035] Examples of the polybasic acid constituting the ester oiliness agent include a dibasic acid and trimellitic acid. The dibasic acid is

preferable from the viewpoint of precipitation prevention properties under a refrigerant atmosphere and a low temperature. The dibasic acid may be either a chain dibasic acid or a cyclic dibasic acid. The chain dibasic acid may be linear or branched, and may be saturated or unsaturated. As the polybasic acid, a chain dibasic acid having 2 to 16 carbon atoms is preferable, and for example, ethanedioic acid, propanedioic acid, butanedioic acid, pentanedioic acid, hexanedioic acid, heptanedioic acid, octanedioic acid, nonanedioic acid, decanedioic acid, and a mixture thereof are preferably used.

[0036] Preferred examples of the ester oiliness agents include glyceryl monooleate, glyceryl dioleate, glyceryl trioleate, and mixtures thereof, sorbitan monooleate, sorbitan dioleate, sorbitan trioleate, and mixtures thereof. Among these, from the viewpoint of more effectively exhibiting low friction in a region where the sliding speed is low, an ester oiliness agent mainly composed of a partial ester is preferable, and glycerin oleate mainly composed of glyceryl monooleate and glyceryl dioleate is particularly preferably used.

[0037] The saponification value of the ester oiliness agent is preferably 100 mgKOH/g or more, more preferably 130 mgKOH/g or more, and is preferably 200 mgKOH/g or less, more preferably 185 mgKOH/g or less, from the viewpoint of more effectively exhibiting low friction in a region where the sliding speed is low. The iodine value of the ester oiliness agent is not particularly limited, but in the case of the oiliness agent having an unsaturated bond, the iodine value is preferably 50 or more, more preferably 60 or more, and is preferably 100 or less, more preferably 80 or less. Here, the saponification value and the iodine value mean a

saponification value and an iodine value measured in accordance with JIS K 0070 (1992).

[0038] Examples of the ether oiliness agent include an etherified product of a tri- to hexa-hydric aliphatic alcohol, and an etherified product of a di- or tri-molecular condensate of a tri- to hexa-hydric aliphatic alcohol.

[0039] Examples of the tri- to hexa-hydric aliphatic alcohol include glycerin, sorbitol, trimethylolpropane, erythritol, pentaerythritol, and the like. Examples of the di- or tri-molecular condensate of a tri- to hexa-hydric aliphatic alcohol include diglycerin, disorbitol, triglycerin, trisorbitol, ditrimethylolpropane, dipentaerythritol, tritrimethylolpropane, and tripentaerythritol.

[0040] Preferred examples of the ether oiliness agents include alkyl or alkenyl glyceryl ethers such as alkyl or alkenyl monoglyceryl ethers and alkyl or alkenyl polyglyceryl ethers having an alkyl or alkenyl group having 4 to 20 carbon atoms, preferably 8 to 18 carbon atoms. More specific examples include lauryl (mono or poly) glyceryl ether, myristyl (mono or poly) glyceryl ether, palmityl (mono or poly) glyceryl ether, stearyl (mono or poly) glyceryl ether, and oleyl (mono or poly) glyceryl ether. A preferred examples include oleyl (mono and di) glyceryl ether.

Such an ether oiliness agent preferably has a hydroxyl group in the molecules thereof from the viewpoint of more effectively exhibiting low friction in a region where the sliding speed is low. The hydroxyl value thereof is preferably 50 mgKOH/g or more, more preferably 100 mgKOH/g or more, still more preferably 200 mgKOH/g or more, and particularly preferably 250 mgKOH/g or more, and is preferably 400 mgKOH/g or less, more preferably 320 mgKOH/g or less. Here, the

hydroxyl value means a hydroxyl value measured in accordance with JIS K 0070 (1992).

5 [0041] The oiliness agent may further contain additional oiliness agents in addition to the ester oiliness agent and the ether oiliness agent described above. Examples of the additional oiliness agent include a monohydric alcohol oiliness agent and a carboxylic acid oiliness agent. Examples of the monohydric alcohol oiliness agent include the monohydric alcohols exemplified in the description of the ester oiliness agent. Examples of the carboxylic acid oiliness agent include the
10 monobasic acids and polybasic acids exemplified in the description of the ester oiliness agent.

[0042] The total content of the oiliness agent, based on the total amount of the refrigerating machine oil, is not particularly limited, but is preferably 0.01% by mass or more, more preferably 0.05% by mass or
15 more, and still more preferably 0.1% by mass or more, from the viewpoint of further improving the frictional properties of the refrigerating machine oil, and is preferably 10% by mass or less, more preferably 5% by mass or less, still more preferably 1% by mass or less, and particularly preferably 0.2% by mass or less, from the viewpoint of preventing
20 precipitation in a refrigerant atmosphere and at low temperatures.

[0043] The refrigerating machine oil according to the present embodiment may further contain additional additives in addition to the respective components described above within a range in which the effects of the present invention are not significantly impaired.
25 Examples of the additional additives include antioxidants, acid scavengers, extreme pressure agents, antifoaming agents, metal

deactivators, antiwear agents, viscosity index improvers, pour point depressants, and detergent dispersants. The content of these additives may be 10% by mass or less or 5% by mass or less based on the total amount of the refrigerating machine oil.

5 [0044] Examples of the antioxidant include a phenol-based antioxidant and an amine-based antioxidant. Examples of the phenol-based antioxidant include 2,6-di-tert.-butyl-p-cresol (DBPC), 2,6-di-tert.-butyl-phenol, and 4,4'-methylene bis(2,6-di-tert.-butyl-phenol). Examples of the amine-based antioxidant include phenyl- α -naphthylamines and
10 dialkylated diphenylamines. These antioxidants may be used alone or in combination of two or more thereof.

[0045] Examples of the acid scavenger include epoxy compounds (epoxy-based acid scavengers). Examples of the epoxy compound include glycidyl ether type epoxy compounds, glycidyl ester type epoxy
15 compounds, aryloxirane compounds, alkyloxirane compounds, cycloaliphatic epoxy compounds, epoxidized fatty acid monoesters, and epoxidized vegetable oils. These acid scavengers can be used alone or in combination of two or more. When the refrigerating machine oil further contains the acid scavenger, the hydrolytic stability can be further
20 improved. This is particularly noticeable when the lubricating base oil contains an ester.

[0046] Examples of the extreme pressure agent include phosphorus-containing extreme pressure agents. Examples of the phosphorus-containing extreme pressure agent include phosphoric acid esters, acidic
25 phosphoric acid esters, amine salts of acidic phosphoric acid esters, chlorinated phosphoric acid esters, phosphorous acid esters,

phosphorothionates, dithiophosphoric acid esters and dithiophosphorylated carboxylic acids. The phosphoric acid ester is preferably triphenyl phosphate (TPP), tricresyl phosphate (TCP), or triphenyl phosphorothionate (TPPT). These extreme pressure agents may be used alone or in combination of two or more.

[0047] As the defoaming agent, any compound usually used as a defoaming agent for a refrigerating machine oil can be used. Examples thereof include silicones such as dimethyl silicones and fluorosilicones. Any one or two or more compounds selected from these compounds can be blended.

[0048] The kinematic viscosity at 40°C of the refrigerating machine oil is preferably 10 mm²/s or less, more preferably 5 mm²/s or less, still more preferably 4 mm²/s or less, from the viewpoint of energy saving and efficiency improvement of the refrigerating machine. The lower limit of the kinematic viscosity at 40°C of the refrigerating machine oil is not particularly limited, and may be, for example, 1 mm²/s or more, or 1.5 mm²/s or more. The kinematic viscosity of the refrigerating machine oil at 100°C may be preferably 0.5 mm²/s or more, more preferably 1 mm²/s or more. The kinematic viscosity of the refrigerating machine oil at 100°C may be preferably 3 mm²/s or less, more preferably 2 mm²/s or less.

[0049] The viscosity index of the refracting machine oil may be 70 or more and may be 200 or less. The viscosity index in the present invention means a viscosity index measured in accordance with JIS K2283:2000.

[0050] The pour point of the refracting machine oil may be preferably be

-10°C or lower, more preferably -20°C or lower.

[0051] The volume resistivity of the refrigerating machine oil may be preferably $1.0 \times 10^9 \Omega \cdot \text{m}$ or more, more preferably $1.0 \times 10^{10} \Omega \cdot \text{m}$ or more, and still more preferably $1.0 \times 10^{11} \Omega \cdot \text{m}$ or more. The volume resistivity in the present invention means a volume resistivity at 25°C measured in accordance with JIS C2101:1999.

[0052] The moisture content of the refrigerating machine oil may be preferably 200 ppm or less, more preferably 100 ppm or less, and still more preferably 50 ppm or less, based on the total amount of the refrigerating machine oil.

[0053] The acid value of the refrigerating machine oil may be preferably 2.0 mgKOH/g or less, more preferably 1.0 mgKOH/g or less, still more preferably 0.1 mgKOH/g or less. The hydroxyl value of the refrigerating machine oil is usually 0 to 100 mgKOH/g, and is preferably 50 mgKOH/g or less, more preferably 20 mgKOH/g or less, and still more preferably 5 mgKOH/g or less.

[0054] The ash content of the refrigerating machine oil may be preferably 100 ppm or less, more preferably 50 ppm or less. The ash content in the present invention means an ash content measured in accordance with JIS K2272:1998.

[0055] The refrigerating machine oil according to this embodiment is usually present in a refrigerating machine and mixed with a refrigerant containing trifluoroiodomethane as a working fluid composition for a refrigerating machine. That is, the working fluid composition for a refrigerating machine according to the present embodiment contains the above-described refrigerating machine oil and a refrigerant. The

content of the refrigerating machine oil in the working fluid composition for a refrigerating machine may be 1 to 500 parts by mass, or 2 to 400 parts by mass, based on 100 parts by mass of the refrigerant.

[0056] Examples of the refrigerant include a hydrocarbon refrigerant, a saturated hydrofluorocarbon refrigerant, an unsaturated hydrofluorocarbon refrigerant, a fluorine-containing ether refrigerant such as perfluoroethers, a bis(trifluoromethyl)sulfide refrigerant, a trifluoroiodomethane refrigerant, and a natural refrigerant such as ammonia and carbon dioxide.

[0057] The hydrocarbon refrigerant is preferably a hydrocarbon having 1 to 5 carbon atoms, more preferably a hydrocarbon having 2 to 4 carbon atoms. Examples of the hydrocarbon include methane, ethylene, ethane, propylene, propane (R290), cyclopropane, normal butane, isobutane (R600a), cyclobutane, methylcyclopropane, 2-methylbutane, normal pentane, and a mixture of two or more thereof. Among them, the hydrocarbon refrigerant is preferably a hydrocarbon refrigerant that is gaseous at 25°C and 1 atm, and more preferably propane, normal butane, isobutane, 2-methylbutane or a mixture thereof is preferably used.

[0058] The saturated hydrofluorocarbon refrigerant is a saturated hydrofluorocarbon having preferably 1 to 3 carbon atoms, more preferably 1 to 2 carbon atoms. Examples of the saturated hydrofluorocarbon refrigerant include difluoromethane (R32), trifluoromethane (R23), pentafluoroethane (R125), 1,1,2,2-tetrafluoroethane (R134), 1,1,1,2-tetrafluoroethane (R134a), 1,1,1-trifluoroethane (R143a), 1,1-difluoroethane (R152a), fluoroethane (R161), 1,1,1,2,3,3,3-heptafluoropropane (R227ea), 1,1,1,2,3,3-

hexafluoropropane (R236ea), 1,1,1,3,3,3-hexafluoropropane (R236fa), 1,1,1,3,3-pentafluoropropane (R245fa), and 1,1,1,3,3-pentafluorobutane (R365mfc), or a mixture of two or more thereof.

[0059] The saturated hydrofluorocarbon refrigerant is appropriately selected from the above depending on the application and the required performance. Examples of the saturated hydrofluorocarbon refrigerant include R32 alone; R23 alone; R134a alone; R125 alone; a mixture of R134a/R32 of 60 to 80% by mass/40 to 20 % by mass; a mixture of R32/R125 of 40 to 70 % by mass/60 to 30 % by mass; a mixture of R125/R143a of 40 to 60 % by mass/60 to 40 % by mass; a mixture of R134a/R32/R125 of 60 % by mass/30 % by mass/10 % by mass; a mixture of R134a/R32/R125 of 40 to 70 % by mass/15 to 35 % by mass/5 to 40 % by mass; and a mixture of R125/R134a/R143a of 35 to 55 % by mass/1 to 15 % by mass/40 to 60 % by mass. More specific examples of the saturated hydrofluorocarbon refrigerant include a mixture of R134a/R32 of 70/30 % by mass; a mixture of R32/R125 of 60/40 % by mass; a mixture of R32/R125 of 50/50 % by mass (R410A); a mixture of R32/R125 of 45/55 % by mass (R410B); a mixture of R125/R143a of 50/50 % by mass (R507C); a mixture of R32/R125/R134a of 30/10/60 % by mass; a mixture of R32/R125/R134a of 23/25/52 % by mass (R407C); a mixture of R32/R125/R134a of 25/15/60 % by mass (R407E); and a mixture of R125/R134a/R143a of 44/4/52 % by mass (R404A).

[0060] The unsaturated hydrofluorocarbon (HFO) refrigerant is preferably an unsaturated hydrofluorocarbon refrigerant having 2 to 3 carbon atoms, more preferably a fluoropropene, still more preferably a fluoropropene having 3 to 5 fluorine atoms. The unsaturated

hydrofluorocarbon refrigerant is preferably any one of 1,2,3,3,3-pentafluoropropene (HFO-1225ye), 1,3,3,3-tetrafluoropropene (HFO-1234ze), 2,3,3,3-tetrafluoropropene (HFO-1234yf), 1,2,3,3-tetrafluoropropene (HFO-1234ye), and 3,3,3-trifluoropropene (HFO-1243zf), or a mixture of two or more thereof. The unsaturated hydrofluorocarbon refrigerant is preferably one or two or more selected from HFO-1225ye, HFO-1234ze and HFO-1234yf are preferable from the viewpoint of the physical properties of the refrigerant. The unsaturated hydrofluorocarbon refrigerant may be a fluoroethylene, and is preferably 1,1,2-trifluoroethylene.

[0061] An example of a refrigerating machine in which the refrigerating machine oil or working fluid composition for a refrigerating machine according to the present embodiment can be suitably used is shown in Fig. 1. Fig. 1 is a schematic diagram illustrating an embodiment of the refrigerating machine. As shown in FIG. 1, the refrigerating machine 10 includes at least a refrigerant circulation system 6 in which a compressor (refrigerant compressor) 1, a condenser (gas cooler) 2, and an expansion mechanism (capillary, expansion valve, etc.) 3 and an evaporator (heat exchanger) 4 are sequentially connected by a flow path 5.

[0062] In the refrigerant circulation system 6, first, the high-temperature refrigerant discharged from the compressor 1 into the flow path 5 becomes a high-density fluid (supercritical fluid or the like) in the condenser 2. Subsequently, the refrigerant is liquefied by passing through the narrow flow path having the expansion mechanism 3, and is further vaporized in the evaporator 4 to have a low temperature. The

cooling by the refrigerating machine 10 utilizes a phenomenon that the refrigerant takes heat from the surroundings when the refrigerant is vaporized in the evaporator 4.

5 [0063] In the compressor 1, a small amount of refrigerant and a large amount of refrigerating machine oil coexist under high temperature conditions. The refrigerant discharged from the compressor 1 to the flow path 5 is in a gaseous state and contains a small amount (usually 1 to 10% by volume) of the refrigerating machine oil as mist, and a small amount of the refrigerant is dissolved in the mist-like refrigerating machine oil (point a in FIG. 1).

[0064] In the condenser 2, the gaseous refrigerant becomes a compressed high-density fluid, and a large amount of the refrigerant and a small amount of the refrigerating machine oil coexist under a relatively high temperature condition (point b in Fig. 1). Further, the mixture of a large amount of refrigerant and a small amount of refrigerating machine oil is sequentially sent to the expansion mechanism 3 and the evaporator 4, rapidly cooled (points c and d in FIG. 1), and returned to the compressor 1 again.

20 [0065] As the compressor 1, a high-pressure container-type compressor in which a motor including a rotor and a stator is accommodated in a closed container storing refrigerating machine oil, a rotary shaft fitted to the rotor, and a compressor unit connected to the motor via the rotary shaft are accommodated, and high-pressure refrigerant gas discharged from the compressor unit stays in the closed container is exemplified.

25 The compressor is not limited to a rotary type such as the compressor 1, and may be a reciprocating type such as a piston-crank type, a screw type,

or a centrifugal type. The hermetic structure of the compressor may be any of an open type, a semi-hermetic type, and a hermetic type, and the hermetic type is particularly preferable.

[0066] The refrigerating machine oil or working fluid composition for a refrigerating machine according to the present embodiment can obtain excellent friction characteristics when used in a refrigerating machine including compressors operated under conditions in which sliding members slide in a region where the sliding speed is low, for example, 0.4 m/s or less, preferably 0.2 m/s or less, more preferably 0.1 m/s or less. The lower limit of the sliding speed is not particularly limited, and may be, for example, 0 m/s or more, and may be 0.001 m/s or more. As such a refrigerating machine, for example, a refrigerating machine such as a refrigerator, a water heater, a freezer, a freezing and refrigerating warehouse, an automatic vending machine, a showcase, or a chemical plant having a reciprocating or rotary hermetic compressor, a refrigerating machine having a centrifugal compressor, or the like is suitable. In the present specification, the "sliding speed" in the compressors is a relative speed when two sliding members slide with slipping, and is represented by the following formula:

$$\text{Sliding speed} = |U_1 - U_2|$$

wherein the speed of the sliding member 1 in the sliding portion is U_1 (m/s) and the speed of the sliding member 2 is U_2 (m/s). Note that in the above formula, U_1 and U_2 may be the same value, and either value may be 0.

Examples

[0067] Hereinafter, the present invention will be described more

specifically based on Examples, but the present invention is not limited to the following Examples.

[0068] (Lubricating base oil)

The following lubricating base oils A1 to A3 were prepared.

5 A1: paraffinic mineral base oil, kinematic viscosity at 40°C: 3.4 mm²/s, kinematic viscosity at 100°C: 1.3 mm²/s, pour point: -35°C, flash point: 131°C, %C_P/%C_N=1.2

A2: paraffinic mineral base oil, kinematic viscosity at 40°C: 2.4 mm²/s, kinematic viscosity at 100°C: 1.0 mm²/s, pour point: -25°C, flash point: 110°C, %C_P/%C_N=1.6

A3: ester-based base oil composed of monoester of 2-ethylhexanol and 2-ethylhexanoic acid and polyolester of neopentyl glycol and 2-ethylhexanoic acid, kinematic viscosity at 40°C: 3.0 mm²/s, acid value: 0.01 mgKOH/g or less, flash point: 140°C

15 [0069] (Refrigerating machine oil)

In Examples and Comparative Examples, the above lubricating base oil and the following components as additives were used to prepare refrigerating machine oils having the composition (% by mass based on the total amount of the refrigerating machine oil) shown in Table 1.

20 [0070] (Oiliness agent)

B1: oleylglyceryl ether (hydroxyl value: 300 mgKOH/g)

B2: sorbitan monooleate (saponification value: 153 mgKOH/g, iodine value: 68)

B3: glycerin monooleate (saponification value: 154 mgKOH/g, iodine value: 70)

[0071] (Other Additives)

C1: mixture of tricresyl phosphate, triphenyl phosphorothionate, and defoaming agent

C2: mixture of glycidyl decanoate and 2, 6-di-tert-butyl paracresol [0072] (Evaluation of friction characteristics)

5 In order to evaluate the friction characteristics of each of the refrigerating machine oils of Examples and Comparative Examples, the following tests were performed.

The friction coefficient (μ) was measured using an MTM (Mini Traction Machine) tester (manufactured by PCS Instruments) under the
10 following conditions. The results are shown in Table 1. The smaller the friction coefficient is, the more excellent the friction characteristics are.

Ball and disc: standard test piece (AISI52100 standard)

Test temperature: 40°C

15 Sliding speed: 0.003, 0.015, 0.03, 0.9 m/s

Applied load: 10N

Sliding ratio: 30%

The sliding speed was a value of $|U_D - U_B|$ (m/s). Here, U_D is the velocity (m/s) of the disk in the sliding portion, and U_B is the velocity
20 (m/s) of the ball in the sliding portion.

[0073] [Table 1]

		Example						Comparative Example		
		1	2	3	4	5	6	1	2	3
Compositon	A1	Balance	Balance	Balance	Balance	Balance	-	Balance	-	-
	A2	-	-	-	-	-	-	-	Balance	-
	A3	-	-	-	-	-	Balance	-	-	Balance
	B1	0.1	0.3	-	-	-	0.3	-	-	-
	B2	-	-	0.5	1.0	-	-	-	-	-
	B3	-	-	-	-	0.3	-	-	-	-
	C1	1.7	1.7	1.7	1.7	1.7	-	1.7	1.7	-
	C2	-	-	-	-	-	0.4	-	-	0.4
Kinematic viscosity (40°C: mm ² /s)		3.4	3.5	3.5	3.5	3.5	3.0	3.4	2.4	3.0
		Friction coefficient (μ)								
Sliding speed (m/s)	0.003	0.093	0.102	0.106	0.108	0.129	0.130	0.136	0.134	0.139
	0.015	0.074	0.081	0.082	0.080	0.090	0.085	0.092	0.098	0.098
	0.03	0.061	0.065	0.064	0.062	0.069	0.063	0.073	0.075	0.071
	0.9	0.022	0.021	0.021	0.019	0.018	0.016	0.025	0.012	0.018

[0074] It was shown that each of the refrigerating machine oils of Examples 1 to 6 had excellent friction characteristics in a low sliding speed region as compared with each of the refrigerating machine oils of Comparative Examples 1 to 3. On the other hand, the refrigerating machine oils of Comparative Examples 1 to 3, which contained neither an ester oiliness agent nor an ether oiliness agent as an additive, had a high friction coefficient in a region where the sliding speed was low. In particular, as shown in Comparative Example 2, even when the kinematic viscosity at 40°C of the refrigerating machine oil was lowered to reduce the viscosity, the friction characteristics in the region where the sliding speed was high were improved, but the friction characteristics in the region where the sliding speed was low were not improved. In the case of the refrigerating machine oil obtained by adding 0.1% by mass of oiliness agent B1 to the refrigerating machine oil of Comparative Example 2, it was observed that the friction coefficient was lowered particularly at a low sliding speed of less than 0.1 m/s.

Reference Signs List

[0075] 1: compressor, 2: condenser, 3: expansion mechanism, 4: evaporator, 5: flow path, 6: refrigerant circulation system, 10: refrigerating machine.

CLAIMS

1. A refrigerating machine oil comprising:
a lubricating base oil having a kinematic viscosity at 40°C of 10 mm²/s or less; and
5 an oiliness agent comprising at least one selected from the group consisting of an ester oiliness agent and an ether oiliness agent.
2. The refrigerating machine oil of claim 1, wherein the lubricating base oil comprises a mineral oil.
3. The refrigerating machine oil according to claim 1 or 2, wherein
10 the oiliness agent comprises the ether oiliness agent.
4. The refrigerating machine oil according to claim 3, wherein the ether oiliness agent is an alkyl or alkenyl glyceryl ether.
5. A working fluid composition for a refrigerating machine, comprising:
15 a refrigerant; and
the refrigerating machine oil according to any one of claims 1 to 4.
6. A refrigerating machine comprising a refrigerant circulation system wherein a compressor, a condenser, an expansion mechanism, and
20 an evaporator are connected by piping in this order, wherein the refrigerant circulation system is filled with a refrigerant and the refrigerating machine oil according to any one of claims 1 to 4.