

DESCRIPTION

Title of Invention: REFRIGERATING MACHINE OIL AND WORKING FLUID COMPOSITION FOR REFRIGERATING MACHINE

5 **Technical Field**

[0001] The present invention relates to a refrigerating machine oil used for a refrigerating machine and a working fluid composition for a refrigerating machine. The "refrigerating machine" as used herein includes air conditioners for automobiles, dehumidifiers, refrigerators, freezing-refrigerating warehouses, vending machines, showcases, cooling apparatus for chemical plants or the like, air conditioners for housing, package air conditioners and heat pumps for supplying hot water.

Background Art

15 [0002] Currently, as a refrigerant for refrigerators, car air conditioners, room air conditioners, industrial refrigerating machines or the like are widely used 1,1,1,2-tetrafluoroethane (R134a), which is one of hydrofluorocarbons (HFC), an R410A which is a mixed refrigerant of difluoromethane (R32) and pentafluoroethane (R125) in a mass ratio of 1/1 and the like. However, the use of these HFC refrigerants is regulated by the so-called F-gas Regulation because they have a high global warming potential (GWP) of 1000 or more although their ozone-depleting potential (ODP) is zero.

25 [0003] As a substitute candidate for a refrigerant with a high GWP, single 2,3,3,3-tetrafluoropropene (HFO-1234yf) or difluoromethane (R32) is studied because of the thermodynamic properties. In addition,

these refrigerants and a mixed refrigerant of them with other refrigerants which have balanced properties with GWP are also studied. It is essential for the substitute for a HFC refrigerant to have a low GWP and HFO-1234yf has a low GWP of 4. R32 has a slightly high GWP of 675, however it is studied as a potential candidate because it has a high gas pressure and is a highly efficient refrigerant.

[0004] Further, hydrocarbon refrigerants such as isobutane (R600a) and propane (R290), which are practically used for refrigerators, have a low GWP of 20 or less and proper physical properties, and therefore are studied although their combustibility, and carbon dioxide (R744), which has a GWP of 1 (standard), is studied as a single refrigerant or a refrigerant to be mixed for the purpose of fireproofing.

[0005] When these refrigerants are used, the working fluid in which a refrigerant and a refrigerating machine oil are mixed together is required to have a higher antiwear property than that of the conventional one because of severe lubrication conditions.

[0006] In general, as an antiwear additive to improve the lubricity of a lubricating oil are known oiliness agents such as alcohols, esters and long-chain fatty acids, antiwear agents such as phosphates, metal dithiophosphates, and extreme-pressure agents such as organic sulfur compounds and organic halogen compounds. In the case of a refrigerating machine oil, alcohol-based or ester-based oiliness agents or triphenyl phosphate or tricresyl phosphate among phosphates are used because they do not precipitate even when coexisting with a refrigerant and only an additive which does not adversely affect stability can be used.

[0007] Furthermore, Patent Literature 1 suggests a lubricating oil including one for refrigerating machine in which a phosphorus-based additive and a specific epoxy compound are added in combination, Patent Literature 2 suggests a lubricating oil for a compressor in which a triphenyl phosphate and a tri(alkylphenyl) phosphate are added in combination for a HFC refrigerant, and Patent Literature 3 suggests a refrigerating machine oil in which a tricresyl phosphate and an epoxy consisting of a glycidyl ether or a carbodiimide are added for a HFC refrigerant.

[0008] However, oiliness agents among these additives form a lubricating film by adsorption, and therefore the friction coefficient can be maintained low in the case of relatively mild loading conditions such as a mixed lubricating area, however the effect of antiwear is lost in the case of severe loading conditions. On the other hand, triphenyl phosphate and tricresyl phosphate have an insufficient antiwear property under severe lubrication conditions in which a refrigerant with a low GWP coexists although they have a certain degree of an antiwear property effect.

[0009] Because of these facts, a refrigerating machine oil with a higher antiwear property is demanded and a working fluid with a high antiwear property in which a refrigerant is mixed is required in a freezing/air conditioning system.

Citation List

Patent Literature

[0010] [Patent Literature 1] Japanese Patent Application Laid-Open No. 5-171174

[Patent Literature 2] Japanese Patent Application Laid-Open No. 8-157847

[Patent Literature 3] Japanese Patent Application Laid-Open No. 9-189453

5 **Summary of Invention**

Technical Problem

 [0011] The present invention was made in view of the above problems, and it is the object of the present invention to provide a refrigerating machine oil and working fluid composition for a refrigerating machine
10 having a high effect of antiwear and being excellent in long-term reliability even under severe lubrication conditions in which a refrigerant coexists.

Solution to Problem

 [0012] The present inventors found that a refrigerating machine oil in
15 which a sulfide compound and a gallate are blended in a base oil and a working fluid for a refrigerating machine consisting of a refrigerant can significantly improve the antiwear property of a refrigerating machine oil without any adverse effect on other properties, and the present invention was completed.

20 [0013] That is, the present invention provides a refrigerating machine oil and working fluid composition for a refrigerating machine according to the following [1] to [9].

 [1] A refrigerating machine oil comprising: a base oil; a sulfide compound; and a gallate, wherein a content of the sulfide compound is
25 0.01 to 2.0% by mass and a content of the gallate is 10 to 500 ppm by mass based on a total amount of the refrigerating machine oil, and the

subjecting a crude oil to atmospheric distillation and further reduced-pressure distillation with means for refining a lubricating oil such as solvent deasphalting, solvent extraction, hydrotreating, hydrocracking, solvent dewaxing, hydrodewaxing and clay treatment in combination appropriately, and can be suitably used. Among them, the solvent extraction, hydrotreating and hydrocracking are processes to control the composition, and the solvent dewaxing and hydrodewaxing to remove the wax component are processes to control low-temperature properties such as a pour point, and the clay treatment is a process to remove the nitrogen component mainly to improve the stability of a base oil. Refined lubricating oil fractions with different characteristics obtained by combining various raw materials with various refining means may be used singly or in combination of two or more.

[0018] Examples of the synthesized oil-based base oil include oxygen-containing compounds such as esters and ethers, hydrocarbon oils such as poly- α -olefins (PAO), ethylene- α -olefin oligomers, alkylbenzenes and alkylnaphthalenes.

[0019] Among the oxygen-containing compounds used as a base oil, esters are compounds having various molecular structures, and are a base oil characterized in they have unique viscosity properties and low-temperature properties respectively and have a higher flash point than that of hydrocarbon-based base oil with the same viscosity. Esters can be obtained by subjecting an alcohol and a fatty acid to dehydration condensation reaction, and in the present embodiment, examples of the suitable base oil component include diesters of a dibasic acid and a monohydric alcohol, polyol esters of a polyol (particularly, a neopentyl

polyol) and a monocarboxylic acid, and complex esters of a polyol, a polybasic acid and a monohydric alcohol (or a monocarboxylic acid) from the viewpoint of chemical stability.

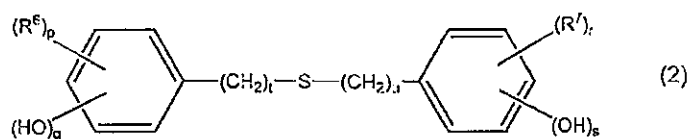
[0020] In the case that an ester is used as the oxygen-containing compound, it is preferable that the ester have the carbon/oxygen molar ratio of 2.5 or more and 5.8 or less from the view point of compatibility with low-GWP refrigerants (such as R32) which have a high polarity. In addition, more preferred are polyol esters which are synthesized from a linear or branched fatty acid with 4 to 9 carbon atoms and a polyhydric alcohol with 4 to 12 carbon atoms and which are excellent in compatibility with various low-GWP refrigerants.

[0021] Specific examples of the linear fatty acid with 4 to 9 carbon atoms include butanoic acid, pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid and nonanoic acid. Specific examples of the branched fatty acid include branched butanoic acids, branched pentanoic acids, branched hexanoic acids, branched heptanoic acids, branched octanoic acids and branched nonanoic acids. More specifically, fatty acids having a branch at the α - and/or β -position are preferable, and 2-methylpropanoic acid, isobutanoic acid, 2-methylbutanoic acid, 2-methylpentanoic acid, 2-methylhexanoic acid, 2-ethylpentanoic acid, 2-methylheptanoic acid, 2-ethylhexanoic acid, 3,5,5-trimethylhexanoic acid and the like are preferable, and among them, 2-methylpropanoic acid, 2-ethylhexanoic acid and/or 3,5,5-trimethylhexanoic acid are the most preferable. Note that fatty acids other than the fatty acids with 4 to 9 carbon atoms may be contained.

[0022] Polyhydric alcohols with 2 to 6 hydroxy groups are preferable as the polyhydric alcohol. Further, it is preferable that the number of carbon atoms of the polyhydric alcohol be 4 to 12. Specifically hindered alcohols such as neopentyl glycol, trimethylolethane, trimethylolpropane, trimethylolbutane, di-(trimethylolpropane), pentaerythritol and di-(pentaerythritol) are preferable. Pentaerythritol or a mixture ester of pentaerythritol and di-(pentaerythritol) is the most preferable because they are excellent in compatibility with refrigerants and hydrolytic stability.

[0023] Among the oxygen-containing compounds used as a base oil, examples of the ether include polyalkylene glycols, compounds in which one end or both ends of a polyalkylene glycol is/are etherified and polyvinyl ethers. Examples of the polyalkylene glycol include polypropylene glycols, polyethylene glycols and copolymers of propylene oxide and ethylene oxide. Compounds in which the hydroxy group at one end is etherified and the hydroxy group at the other end is remained is typical, however, compounds in which the both ends are etherified is preferable because they have a low hygroscopicity, and with regard to the backbone, an oxypropylene type is more preferred than an oxyethylene type which has a high hygroscopicity. In the case of etherifying the end, an alkyl group with 1 to 4 carbon atoms is preferable from the view point of compatibility with refrigerants and the smaller the number of carbon atoms is, the better the compatibility becomes. In view of compatibility, stability, electrical insulation properties, low hygroscopicity or the like, polypropylene glycols in which the both ends are methyl-etherified are

[Chemical Formula 2]



[R⁶ and R⁷ may be identical to or different from each other and each represents a hydrocarbon group; p, q, r and s may be identical to or different from each other and each represents an integer of 0 to 5 such that p+q and r+s are 0 to 5, with the proviso that at least one of q and s is 1 or more; and t and u may be identical to or different from each other and each represents an integer of 0 to 10.]

[0030] In the formula (2), R⁶ and R⁷ may be identical to or different from each other and each represents a hydrocarbon group, and p, q, r and s may be identical to or different from each other and each represents an integer of 0 to 5 such that p+q and r+s are 0 to 5. However, at least one of q and s is 1 or more and most preferably both of q and s are 1. Further, t and u may be identical to or different from each other and each represents an integer of 0 to 10. t and u are preferably 0 to 4, more preferably both of t and u are 0 or 1, and most preferably both of t and u are 0. A preferred hydrocarbon group is an alkyl group, cycloalkyl group and alkenyl group with 1 to 10 carbon atoms, preferably with 1 to 6 carbon atoms and phenyl group, and specific examples thereof include a methyl group, an ethyl group, an n-propyl group, an i-propyl group, an n-butyl group, a sec-butyl group and a tert-butyl group.

[0031] Preferred examples of the compound represented by the formula (2) specifically include 4,4'-thiobis(3-methyl-6-tert-butylphenol),

4,4'-thiobis(2,6-di-tert-butylphenol),
4,4'-thiobis(2-methyl-6-tert-butylphenol),
2,2'-thiobis(4-methyl-6-tert-butylphenol),
2,2'-thiobis(4,6-di-tert-butylphenol) and
5 bis(3,5-di-tert-butyl-4-hydroxybenzyl)sulfide.

[0032] The content of the sulfide compound is 0.01 to 2% by mass, preferably 0.05 to 1% by mass, and more preferably 0.1 to 0.5% by mass based on the total amount of the refrigerating machine oil. The above range is preferable because the antiwear property-improving effect is high and the corrosive wear due to an atmosphere may not be caused.

[0033] With regard to the gallate in the present embodiment, gallic acid is an aromatic carboxylic acid in which three hydroxy groups are bonded to an aromatic ring, and also known as 3,4,5-trihydroxybenzoic acid. And an ester obtained by the reaction of gallic acid and an alcohol is a gallate (gallic acid ester). Examples of the gallate include methyl gallate, ethyl gallate, propyl gallate, isoamyl gallate, octyl gallate and dodecyl gallate, and some of them are used as a food additive. Compounds whose alkyl group has 1 to 18 carbon atoms are preferable as the gallate in the present embodiment, and when the alkyl group has more than 18 carbon atoms, the effect of antiwear is lowered. Esters of gallic acid and an alcohol with 1 to 8 carbon atoms are more preferable and ethyl gallate and propyl gallate are the most preferable.

[0034] The content of the gallate is 10 to 500 ppm by mass, preferably 10 to 100 ppm by mass based on the total amount of the refrigerating machine oil. By setting the content to the above range, a high stability

and a sufficient antiwear property-improving effect can be obtained without precipitation at a low temperature due to the reduction of solubility in a base oil.

[0035] In the present embodiment, the refrigerating machine oil can further contain an orthophosphate as an antiwear additive.

[0036] Preferred compounds as the orthophosphate include triphenyl phosphate (TPP), tricresyl phosphate (TCP) and alkylphenyl phosphates (APP) having an alkyl group with 3 to 4 carbon atoms. TPP and TCP have a single structure and an APP is a mixture of one having one alkylphenyl (mono-type), one having two alkylphenyls (di-type) and one having three alkylphenyls (tri-type), however, the ratio thereof is not particularly limited.

[0037] The content of the orthophosphate is preferably 0.05 to 3% by mass, more preferably 0.1 to 2% by mass, and further preferably 0.2 to 1.5% by mass based on the total amount of the refrigerating machine oil. By setting the content to the above range, a sufficient antiwear property-improving effect and a high stability can be obtained.

[0038] In the present embodiment, the antiwear property of the working fluid is significantly improved by further blending pentaerythritol tetra(2-ethylhexanoate) in the refrigerating machine oil. Pentaerythritol tetra(2-ethylhexanoate) is an ester synthesized from pentaerythritol and 2-ethylhexanoic acid. It is desirable that it be a complete ester (also referred to as a "full ester") in which all of the hydroxyl groups in the pentaerythritol are esterified. It is preferable that the acid value of the ester be 0.1 mgKOH/g or less and the hydroxyl value thereof be 10 mgKOH/g or less, respectively. The amount of the

150 mm²/s. By setting the kinematic viscosity in the above range, a sufficient antiwear property can be obtained and compatibility with a refrigerant can be enhanced.

5 [0042] The characteristics of the refrigerating machine oil other than the kinematic viscosity at 40°C are not particularly limited, however, the viscosity index is preferably 10 or more. The pour point is preferably -10°C or lower, and more preferably -20°C or lower. The flash point is preferably 120°C or higher, and more preferably 200°C or higher.

10 [0043] In addition, the acid value of the refrigerating machine oil is not particularly limited, however, in order to prevent the corrosion of metals used in a refrigerating machine or a piping and suppress the deterioration of the refrigerating machine oil itself, the acid value can be preferably set to 0.1 mgKOH/g or less, and more preferably 0.05
15 mgKOH/g or less. Note that the acid value in the present invention means an acid value measured in accordance with JIS K2501 "Petroleum products and lubricants-Determination of neutralization number".

[0044] The moisture content of the refrigerating machine oil is not
20 particularly limited, however, it is preferably 200 ppm or less, more preferably 100 ppm or less, and most preferably 50 ppm or less. Particularly in the case that the refrigerating machine oil is used for a sealed-type refrigerating machine, the moisture content is required to be low from the viewpoint of the stability and electrical insulation
25 properties of the refrigerating machine oil.

[0045] With regard to refrigerating machines, there is a trend that the

low GWP and difluoromethane (R32), or hydrocarbon refrigerants such as isobutane (R600a) and propane (R290), carbon dioxide (R744), and in addition mixed refrigerants containing them are studied and considered to be leading candidates.

5 [0048] Examples of the unsaturated hydrocarbon include 2,3,3,3-tetrafluoropropene (HFO-1234yf), 1,3,3,3-tetrafluoropropene (HFO-1234ze) and 1,2,3,3,3-pentafluoropropene (HFO-1225ye). These HFO refrigerants have an olefin structure subject to decomposition in the molecule, and therefore characterized in that they
10 have a low stability, although having a low GWP. In particular, under conditions of a high loading, a local heat generation occurs at a sliding part of metal/metal contact to cause the decomposition of the refrigerant to be accelerated along with wear and hydrofluoric acid is generated, which may lead to the deterioration of the working fluid in which the
15 refrigerant and the refrigerating machine oil are mutually dissolved and moreover may cause corrosive wear in relation to lubricity, and therefore the lubricity of the refrigerating machine oil is critical properties.

[0049] In the case of R32 which is a hydrofluorocarbon (HFC) having a
20 low boiling point and a high pressure or a mixed refrigerant containing a large amount of R32, the discharge temperature of the compressor is increased to reduce the thickness of the oil film of the refrigerating machine oil, resulting in severe lubrication conditions. In the case of a hydrocarbon refrigerant, it has no fluorine in the hydrocarbon molecule,
25 which contributes to the improvement of lubricity, and has a high solubility in the refrigerating machine oil, which lowers the viscosity of

the refrigerating machine oil, resulting in severe lubrication conditions. As described above, any of the refrigerant candidates having a low GWP causes severe conditions in view of lubricity, and therefore the refrigerating machine oil to be used is required to have a high lubricity.

5 [0050] The refrigerant in the present embodiment is not particularly limited, however, a refrigerant which dissolves mutually, that is, a refrigerant which dissolves mutually without being separated into two layers at a normal temperature is preferable. Further, from the aspect of the environmental protection, a refrigerant having a global warming
10 potential (GWP) of 700 or less is preferable, a refrigerant containing one or more selected from a hydrofluorocarbon (HFC), a hydrofluoroolefin (HFO), carbon dioxide (R744) and a hydrocarbon with 2 to 4 carbon atoms is more preferable, and a refrigerant containing difluoromethane (R32) and/or 2,3,3,3-tetrafluoropropene (HFO-1234yf)
15 is the most preferable.

[0051] In the working fluid composition for a refrigerating machine according to the present embodiment, the blending ratio of the refrigerating machine oil/refrigerant is not particularly limited, however, the blending ratio is usually 1 to 1000 parts by weight, and preferably 2
20 to 800 parts by weight based on 100 parts by weight of the refrigerant.

Examples

[0052] Hereinafter, the present invention will be specifically described on the basis of Examples and Comparative Examples, however, the present invention is never limited to the following Examples.

25 [0053] [Examples 1 to 12, Comparative Examples 1 to 10]

In Examples 1 to 12 and Comparative Examples 1 to 10,

Note that the kinematic viscosity and the viscosity index were measured in accordance with JIS K2283, the pour point was measured in accordance with JIS K2269, and the flashing point was measured in accordance with JIS K2265.

5 [0055] [Sulfide Compound]

(S-1) Dibenzyl sulfide

(S-2) Didodecyl sulfide

(S-3) 4,4'-thiobis (3-methyl-6-tert-butylphenol)

[0056] [Gallate]

10 (G-1) Propyl gallate (n-propyl gallate)

(G-2) Octyl gallate (n-octyl gallate)

[0057] [Orthophosphate]

(P-1) Tricresyl phosphate (TCP)

[0058] [Other Base Blending Material]

15 (D-1) Pentaerythritol tetra(2-ethylhexanoate) (an ester of pentaerythritol and 2-ethylhexanoic acid; acid value: 0.01 mgKOH/g; hydroxyl value: 1.2 mgKOH/g)

[0059] Next, the refrigerating machine oils in Examples 1 to 12 and Comparative Examples 1 to 10 were subjected to the following lubricity
20 test and stability test in combination with the various refrigerants shown in Tables 1 to 3. Note that "1234yf" in Tables 1 to 3 means HFO-1234yf.

[0060] (Lubricity Test)

25 The lubricity test was in accordance with ASTM D3233-73 and the wear test was carried out with a Falex (pin/V-block) test machine at a constant loading.

	- -	- -	1.0 -	- 3.0	- -	- -	- -	1.0 -
	50 -	50 -	- 50	50 -	50 -	50 -	- 50	50 -
	68.2	68.2	68.3	65.9	66.8	66.9	46.2	65.5
	R32 3.2	R32 3.0	R32 1.6	R32 1.8	1234yf 3.6	R600a 2.8	R32 2.2	R32 1.6
	R32 No precipitation 0.01	R32 No precipitation 0.01	R32 No precipitation 0.01	R32 No precipitation 0.01	1234yf No precipitation 0.03	R600a No precipitation 0.01	R32 No precipitation 0.01	R32 No precipitation 0.01

[0063] [Table 2]

	Example 9	Example 10	Example 11	Example 12	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4
<Base oil> Type	A-5	A-3	A-4	A-5	A-1	A-3	A-1	A-1
Content ratio (% by mass)	99.8	99.8	99.8	99.8	100	100	99.8	99.5
<Additive or base blending material> (% by mass)								
S-1	0.2	-	-	-	-	-	0.2	-
S-2	-	-	-	-	-	-	-	-
S-3	-	0.2	0.2	0.2	-	-	-	0.5
P-1	-	-	-	1.0	-	-	-	-
D-1	-	-	-	-	-	-	-	-
<Additive> (ppm by mass)								
G-1	20	30	100	-	-	-	-	-
G-2	-	-	-	20	-	-	-	-
Kinematic viscosity at 40°C of refrigerating machine oil (mm ² /s)	22.4	46.1	66.5	22.3	68.1	46.0	68.1	68.2
<Lubricity test> Refrigerant	R600a	1234yf	1234yf	R600a	R32	1234yf	R32	R32
Amount of wear (mg)	3.1	3.9	3.3	2.0	12.3	14.5	8.2	7.6
<Thermal stability test> Refrigerant	R600a	1234yf	1234yf	R600a	R32	1234yf	R32	R32
Appearance	No precipitation	No precipitation	No precipitation	No precipitation	No precipitation	No precipitation	No precipitation	No precipitation
Acid value (mgKOH/g)	0.01	0.03	0.03	0.01	0.01	0.03	0.01	0.01

	- - -	- -	1.0 -	0.2 1.0 -	- - -	0.2 1.0 -
	50 -	1000 -	- -	- -	- -	- -
	66.7	46.2	45.9	22.3	68.2	68.0
	R32 8.6	1234yf 4.6	R32 7.0	R600a 6.8	R32 6.9	R32 6.5
	R32 No precipitation 0.01	1234yf Precipitation 0.12	R32 No precipitation 0.01	R600a No precipitation 0.01	R32 No precipitation 0.01	R32 No precipitation 0.01

CLAIMS

1. A refrigerating machine oil comprising:

a base oil;

a sulfide compound; and

5 a gallate,

wherein a content of the sulfide compound is 0.01 to 2.0% by mass and a content of the gallate is 10 to 500 ppm by mass based on a total amount of the refrigerating machine oil, and

10 the refrigerating machine oil having a kinematic viscosity at 40°C of 3 to 500 mm²/s.

2. The refrigerating machine oil according to claim 1, wherein the base oil is at least one selected from an ester with a carbon/oxygen molar ratio of 2.5 or more and 5.8 or less and an ether with a carbon/oxygen molar ratio of 2.5 or more and 5.8 or less; and the
15 kinematic viscosity of the refrigerating machine oil at 40°C is 3 to 300 mm²/s.

3. The refrigerating machine oil according to claim 1, wherein the base oil is at least one selected from a polyol ester obtainable by synthesis of a fatty acid with 4 or more and 9 or less carbon atoms and a
20 polyalcohol with 4 or more and 12 or less carbon atoms, a polyalkylene glycol, a compound in which hydroxyl groups at both ends of a polyalkylene glycol are etherified, and a polyvinyl ether.

4. The refrigerating machine oil according to claim 1, further comprising 0.05 to 3% by mass of an orthophosphate based on the total
25 amount of the refrigerating machine oil.

5. The refrigerating machine oil according to claim 1, wherein the

sulfide compound is a thiobisphenol compound and the gallate has an alkyl group with 1 to 18 carbon atoms.

6. The refrigerating machine oil according to claim 1, further comprising 2 to 20% by mass of pentaerythritol tetra(2-ethylhexanoate) based on the total amount of the refrigerating machine oil.

7. A working fluid composition for a refrigerating machine consisting of:

a refrigerant with a global warming potential of 700 or less; and
the refrigerating machine oil according to claim 1.

8. The working fluid composition for a refrigerating machine according to claim 7, wherein the refrigerant is a refrigerant comprising at least one selected from a hydrofluorocarbon, a hydrofluoroolefin, carbon dioxide and a hydrocarbon with 2 to 4 carbon atoms.

9. The working fluid composition for a refrigerating machine according to claim 7, wherein the refrigerant is a refrigerant comprising at least one selected from difluoromethane and 2,3,3,3-tetrafluoropropene.