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(54) Lubricating oil composition for refrigeration machine.

(57) Disclosed is a lubricating oil composition for refrigeration machine comprising 100 parts by weight of a carboxylic ester having a number-average molecular weight (Mn) of 200 to 5,000 and a kinematic viscosity at 100 °C of 2 to 100 cSt or a carbonic ester having a number-average molecular weight (Mn) of 200 to 5,000 and a kinematic viscosity at 100 °C of 2 to 100 cSt, and 0.001 to 15 parts by weight of a fluoroalkyl group-containing alcohol. The lubricating oil composition for refrigeration machine can extremely reduce the amount of metal abrasion at the slide part of the compression type refrigeration machine in which hydrogenated fluorocarbon (HFC) such as R-134a is used as a refrigerant. This composition can be also used for refrigeration machines of other types than the compression type because of its excellent lubricating properties.

FIELD OF THE INVENTION

The present invention relates to a lubricating oil composition for refrigeration machines, and more particularly to a lubricating oil composition which is used for compression type refrigeration machines of automotive air-conditioners, electric refrigerators and room air conditioners, wherein hydrogenated fluorocarbon (HFC) is used as a refrigerant.

BACKGROUND OF THE INVENTION

Chlorofluorocarbons (CFC) such as R-12 (CCl_2F_2) or hydrogenated chlorofluorocarbons (HCFC) such as R-22 ($CHClF_2$) have been heretofore used as refrigerants for compression type refrigeration machines used in automotive air-conditioners, electric refrigerators for domestic use, room air-conditioners, etc., but recently, these refrigerants, which contain chlorine, can be hardly used for those purposes from the viewpoint of prevention of ozone layer destruction.

Now, hydrogenated fluorocarbons (HFC) such as 1,1,1,2-tetrafluoroethane (R-134a) have been developed as ozone layer-nondestructive refrigerants. Examples of lubricating oils for refrigeration machines developed as the HFC include polyalkylene glycol and derivatives thereof, carboxylic ester derivatives and carbonic ester derivatives.

Japanese Patent Laid-Open Publication No. 12497/1991 describes that a lubricating oil composition comprising a fluoroalkyl group-containing alcohol represented by the following formula and a polyether compound shows good compatibility with HFC and is excellent in anti-burning properties.

$R_f\text{-}R^1\text{-}OH$

wherein R^1 is an alkylene group of 2 to 15 carbon atoms, R_f is a fluoroalkyl group of 5 to 16 carbon atoms, the number of fluorine atoms in the R_f group is at least 2n-3 (n is the number of carbon atoms in the R_f group), and at least one fluorine atom is bonded to each carbon atom in the R_f group.

With regard to the compression type refrigeration machines for automotive air-conditioners, electric refrigerators for domestic use, etc., there has been recently proposed a novel refrigerating system as an ozone layer-nondestructive system, that is, a refrigerating apparatus system in which HFC such as R-134a is used as a refrigerant, a lubricating oil comprising polyalkylene glycol or its derivative, a carboxylic ester derivative, a carbonic ester derivative or the like is used, and the refrigerating apparatus is made of a material suitable for the lubricating oil.

However, this novel system involves such problems that when repeated endurance tests are conducted, the amount of metal abrasion is large at the slide part of the compression type refrigeration machine and the abrasion resistance of the slide part is insufficient.

Accordingly, it has been desired to develop a lubricating oil for refrigeration machine which can prominently reduce the amount of metal abrasion at the slide part of the compression type refrigeration machine where hydrogenated fluorocarbon such as R-134a is used as a refrigerant.

OBJECT OF THE INVENTION

The present invention is intended to solve such problems associated with the prior art technique as mentioned above, and it is an object of the invention to provide a lubricating oil composition for refrigeration machine which can prominently reduce the amount of metal abrasion at the slide part of the compression type refrigeration machine where hydrogenated fluorocarbon such as R-134a is used as a refrigerant.

SUMMARY OF THE INVENTION

The lubricating oil composition for refrigeration machine according to the invention comprises:

100 parts by weight of a carboxylic ester having a number-average molecular weight (Mn) of 200 to 5,000 and a kinematic viscosity at 100 °C of 2 to 100 cSt or a carbonic ester having a number-average molecular weight (Mn) of 200 to 5,000 and a kinematic viscosity at 100 °C of 2 to 100 cSt, and

0.001 to 15 parts by weight of a fluoroalkyl group-containing alcohol.

The molecular weight of the fluoroalkyl group-containing alcohol is preferably in the range of 30 to 2,000.

The lubricating oil composition of the invention is preferably used for compression type refrigeration machines, particularly those where hydrogenated fluorocarbon (HFC) is used as a refrigerant.

DETAILED DESCRIPTION OF THE INVENTION

The lubricating oil composition for refrigeration machine according to the invention will be described in detail hereinafter.

The lubricating oil composition for refrigeration machine according to the invention comprises a carboxylic ester having a specific number-average molecular weight (Mn) and a specific kinematic viscosity or a carbonic ester having a specific number-average molecular weight (Mn) and a specific kinematic viscosity, and a fluoroalkyl group-containing alcohol, in specific amounts.

The carboxylic ester or the carbonic ester is used as a base oil for a lubricating oil.

Carboxylic ester

The carboxylic ester used in the invention has at least one ester group in the molecule, and has a number-average molecular weight (Mn), as determined by GPC, of 200 to 5,000, preferably 300 to 4,000, more preferably 300 to 3,000. This carboxylic ester has a kinematic viscosity at 100 °C of 2 to 100 cSt, preferably 2.5 to 80 cSt, more preferably 3.0 to 70 cSt.

In the present invention, carboxylic esters described in, for example, the following publications can be used.

Japanese Patent Laid-Open Publication No. 227397/1991 describes carboxylic esters obtained from fatty acids of 2 to 6 carbon atoms (e.g., butanoic acid, 2-methylpropanoic acid, pentanoic acid, 2-methylbutanoic acid, 3-methylbutanoic acid, hexanoic acid, 2-ethylbutanoic acid, 2-methylpentanoic acid and mixtures thereof) and neopentyl polyols (e.g., pentaerythritol, dipentaerythritol, tripentaerythritol, tetrapentaerythritol, ditrimethylolpropane and mixtures thereof). Examples of such carboxylic esters include neopentyl di-2-methylhexoate, neopentyl dibutyrate, neopentyl dicaproate and neopentyl dienanthate. Of these, preferred is neopentyl di-2-methylhexoate.

Japanese Patent Laid-Open Publication No. 128991/1991 describes a carboxylic ester obtained from at least one divalent alcohol of 5 to 12 carbon atoms which has no ether linkage and at least one straight- or branched-chain monovalent fatty acid of 3 to 18 carbon atoms, and a carboxylic ester obtained from at least one divalent alcohol of 5 to 12 carbon atoms which has no ether linkage, at least one straight- or branched-chain monovalent fatty acid of 3 to 18 carbon atoms and at least one polybasic acid of 4 to 14 carbon atoms. Examples of such carboxylic esters include 2,2-dimethyl-1,3-propanediol dicaproate, 2-butyl-2-ethyl-1,3-propanediol dicaproate, 2,2-dimethyl-3-methylpentoate and 3-methyl-1,5-pentanediol di-2-methylhexoate. Of these, particularly preferred are 2,2-dimethyl-3-methylpentoate and 3-methyl-1,5-pentanediol di-2-methylhexoate.

Examples of the divalent alcohols of 5 to 12 carbon atoms which have no ether linkage include neopentyl glycol, 2,2-diethyl-1,3-propanediol, 2-butyl-2-ethyl-1,3-propanediol, 3-methyl-1,5-pentanediol, 2,2,4-trimethyl-1,3-pentanediol and 2-ethyl-1,3-hexanediol.

Examples of the straight- or branched-chain monovalent fatty acids of 3 to 18 carbon atoms include propionic acid, isopropionic acid, butanoic acid, isobutanoic acid, pentanoic acid, hexanoic acid, heptanoic acid, isoheptanoic acid, octanoic acid, 2-ethylhexanoic acid, nonanoic acid, 3,5,5-trimethylhexanoic acid, decanoic acid, undecanoic acid, lauric acid, myristic acid, palmitic acid, stearic acid, isostearic acid, oleic acid, linoleic acid and linolenic acid.

Examples of the polybasic acids of 4 to 14 carbon atoms include succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, phthalic acid and maleic acid.

Further, Japanese Patent Laid-Open Publications No. 20597/1992, No. 217493/1991 and No. 128992/1991 describe carboxylic esters obtained from polyhydric alcohols (e.g., trimethylolethane, trimethylolpropane, pentaerythritol and neopentyl glycol) and monocarboxylic acids (e.g., 2-ethylhexanoic acid, heptanoic acid and caproic acid) or derivatives thereof. Examples of such carboxylic esters include:

(1) triester composed of trimethylolpropane (1 mol) and 2-ethylhexanoic acid (3 mol), which is represented by the formula:

$$C_2H_5C[CH_2OOCCH_2(C_2H_5)(CH_2)_3CH_3]_3,$$

(2) triester composed of trimethylolpropane (1 mol) and 3,5,5-trimethylhexanoic acid, which is represented by the formula:

$$C_2H_5C[CH_2OOCCH_2CH(CH_3)CH_2C(CH_3)_3]_3,$$

(3) triester composed of trimethylolpropane (1 mol), 2-ethylhexanoic acid (1.5 mol) and 3,3,5-trimethylhexanoic acid (1.5 mol),

(4) tetraester composed of di(trimethylolpropane) (1 mol), n-hexanoic acid (2 mol) and 2,4-dimethylpentanoic acid (2 mol), which is represented by the formula:

$[RCOOCH_2]_2C(C_2H_5)CH_2OCH_2C(C_2H_5)[CH_2OCOR]_2$

(wherein R is $-(CH_2)_4CH_3$ or $-CH(CH_3)CH_2CH-(CH_3)_2)$, and

(5) tetraester composed of di(trimethylolpropane) (1 mol) and 3,3,5-trimethylhexanoic acid (4 mol), which is represented by the formula:

$[RCOOCH_2]_2C(C_2H_5)CH_2OCH_2C(C_2H_5)[CH_2OCOR]_2$

(wherein R is $-CH_2CH(CH_3)CH_2C(CH_3)_3$).

Of the carboxylic esters obtained from polyhydric alcohols and monocarboxylic acids or derivatives thereof, preferred are the carboxylic esters (1) to (5), and particularly preferred are the carboxylic esters (2), (4) and (5).

Examples of other carboxylic esters than the carboxylic esters (1) to (5) include pentaerythritol tetrabutyrate, pentaerythritol tetravalerate, pentaerythritol tetracaproate, pentaerythritol tetraenanthate, pentaerythritol tetra-2-methylhexoate and pentaerythrltol tetra-2,2-dimethyl-3-methylpentoate. Of these, preferred are pentaerythritol tetrabutyrate, pentaerythritol tetravalerate, pentaerythritol tetracaproate, pentaerythritol tetra-2-methylhexoate and pentaerythritol tetra-2,2-dimethyl-3-methylpentoate; and particularly preferred are pentaerythritol tetra-2-methylhexoate and pentaerythritol tetra-2,2-dimethyl-3-methylpentoate.

Moreover, National Publication of International Patent No. 505602/1991 describes carboxylic esters obtained from polyhydroxy compounds containing at least two hydroxyl groups and carboxylic acids.

Examples of the polyhydroxy compounds include ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol, glycerol, neopentyl glycol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol, pentaerythritol, dipentaerythritol, tripentaerythritol, triglycerol, trimethylolpropane and sorbitol.

Examples of the carboxylic acids include straight-chain saturated monocarboxylic acids such as formic acid, acetic acid, propionic acid, butyric acid, pentanoic acid, hexanoic acid and heptanoic acid; branched-chain saturated monocarboxylic acids such as 2-ethyl-n-butyric acid, 2-hexyldecanoic acid, isostearic acid, 2-methylhexanoic acid, 3,5,5-trimethylhexanoic acid, 2-ethylhexanoic acid, neoheptanoic acid and neodecanoic acid; saturated dicarboxylic acids such as succinic acid; and unsaturated dicarboxylic acids such as maleic acid.

Examples of such carboxylic esters as mentioned above include sorbitol hexabutyrate and sorbitol hexavalerate.

If the carboxylic esters described hereinbefore are arranged in order of preferability, there are arranged the carboxylic esters described in National Publication of International Patent No. 505602/1991, the carboxylic esters described in Japanese Patent Laid-Open Publication Nos. 20597/1992, 217493/1991 and 128992/1992, the carboxylic esters described in Japanese Patent Laid-Open Publication No. 128991/1991 and the carboxylic esters described in Japanese Patent Laid-Open Publication No. 227397/1991 in this order.

Carbonic ester

The carbonic ester used in the invention has at least one carbonate group in the molecule, and has a number-average molecular weight (Mn), as determined by GPC, of 200 to 5,000, preferably 300 to 4,000, more preferably 300 to 3,000. This carbonic ester has a kinematic viscosity at 100 °C of 2 to 100 cSt, preferably 2.5 to 80 cSt, more preferably 3.0 to 70 cSt.

Examples of such carbonic esters include those obtained from aliphatic alcohols having 1 to 6 primary hydroxyl groups (e.g., trimethylolethane, trimethylolpropane and neopentyl glycol) and lower esters of carbonic acids (e.g., dimethyl carbonate, diethyl carbonate, diphenyl carbonate, ethylene carbonate and propylene carbonate) or carbonyl halides (e.g., phosgene). More specifically, there can be mentioned 3-methyl-1,5-pentamethylene di(methylhexylcarbonate), 3-ethyl-3-butyl-1,5-pentamethylene di(methylhexylcarbonate), etc. These carbonic esters are described in Japanese Patent Laid-Open Publication No. 217498/1991.

Other examples of the carbonic esters are the following compounds, which are described in Japanese Patent Laid-Open Publication No. 18490/1992.

(1) Compounds of the formula $(ROCOOCH_2)_4C$ wherein R is iso-C_6H_{13} or iso-C_7H_{15},
(2) Compounds of the formula $(ROCOOCH_2)_3CCH_3$ wherein R is iso-C_6H_{13} or iso-C_7H_{15}, and
(3) Compounds of the formula $(ROCOOCH_2)_3CCH_2OCH_2C(CH_2OCOOR)_3$ wherein R is iso-C_3H_7 or iso-C_4H_9.

Other than the carbonic esters mentioned above, there can be also used glycol ether carbonates described in Japanese Patent Laid-Open Publication No. 247695/1991, which are represented by the following formula:

R_1-O-[(R_3)O]$_n$-COO-R_2

wherein R_1 and R_2 are each independently an aliphatic, alicyclic, aromatic or aromatic-aliphatic hydrocarbon group of 1 to 20 carbon atoms, R_3 is an ethylene group or a propylene group, and n is an integer of 2 to 100.

Examples of the glycol ether carbonates represented by the above formula include compounds of the following formulas:

(1) CH_3-[C_3H_6O]-COO-$C_3H_6CH_3$

(2) n-C_4H_9O-[C_3H_6O]$_n$-COO-CH_3

wherein n is an integer of 2 to 100, preferably an integer of 5 to 90, more preferably an integer of 10 to 60.

Further, there can be used polycarbonates derived from sugar such as sorbitol, and polycarbonates having no cyclic structure and represented by the following formula:

CH_3-O-[C_3H_6O]$_n$-COO-[C_3H_6O]$_n$$CH_3$

wherein n is an integer of 2 to 100, preferably an integer of 3 to 90, more preferably an integer of 5 to 60.

Of the carbonic esters mentioned above, preferably used are the glycol ether carbonates of the above formula which are described in Japanese Patent Laid-Open Publication No. 247695/1991, polycarbonates derived from sugar such as sorbitol and polycarbonates of the above formula which have no cyclic structure.

If the carbonic esters described hereinbefore are arranged in order of preferability, there are arranged the glycol ether carbonates of the above formula which are described in Japanese Patent Laid-Open Publication No. 247695/1991, the polycarbonates derived from sugar such as sorbitol, the polycarbonates of the above formula which have no cyclic structure and the carbonic esters described in Japanese Patent Laid-Open Publication No. 217498/1991 in this order.

Fluoroalkyl group-containing alcohol

The fluoroalkyl group-containing alcohol used in the invention has a molecular weight of usually 30 to 2,000, preferably 50 to 1,000, more preferably 100 to 900.

Examples of the fluoroalkyl group-containing alcohols include monovalent fluoroalkyl group-containing alcohols such as trifluoroethanol, perfluorohexyl ethyl alcohol, perfluorooctyl ethyl alcohol, perfluorodecyl ethyl alcohol, 1H,2H,5H-octafluoropentanol and hexafluoroisopropanol; and divalent fluoroalkyl group-containing alcohols such as 3-(2-perfluorohexyl)ethoxy-1,2-dihydroxypropane and N-n-2,3-dihydroxypropylperfluorooctyl sulfonamide. Of these, preferably used are perfluorohexyl ethyl alcohol, perfluorooctyl ethyl alcohol and perfluorodecyl ethyl alcohol.

These fluoroalkyl group-containing alcohols are used singly or in combination.

In the present invention, the fluoroalkyl group-containing alcohol is used in an amount of 0.001 to 15 parts by weight, preferably 0.1 to 10 parts by weight, more preferably 1 to 8 parts by weight, based on 100 parts by weight of the carboxylic ester or the carbonic ester.

When the fluoroalkyl group-containing alcohol is used in the above-defined amount, the amount of metal abrasion at the slide part of the compression type refrigeration machine in which HFC such as R-134a is used as a refrigerant can be extremely reduced. Moreover, the carboxylic ester or the carbonic ester can be prevented from being lowered in the solubility, and the lubricating oil composition for refrigeration machine can be prevented from being greatly decreased in the kinematic viscosity.

The lubricating oil composition for refrigeration machine according to the invention is very economical because the expensive fluoroalkyl group-containing alcohol is used in a relatively small amount as described above.

The lubricating oil composition for refrigeration machine according to the invention may further contain conventionally known abrasion decreasing agents, in addition to the carboxylic ester or the carbonic ester as the base oil for the lubricating oil and the fluoroalkyl group-containing alcohol as the additive.

Examples of such abrasion decreasing agents include phosphoric esters; acidic phosphoric esters; amine salts of acidic phosphoric esters; fatty acids; monoalcohols such as decanol, lauryl alcohol, 2-ethylhexanol and 2-ethyl-1,3-hexanediol; polyhydric alcohols such as 1,2-decanediol, 1,2-octanediol, triethylene glycol and diethylene glycol; dimethyl ether of ethylene oxide/propylene oxide block copolymer; carbamic esters; zinc dithiophosphate; carboxylates; sulfites; mercaptans; and alkylpolysiloxane fluorides. These abrasion decreasing agents may be used singly or in combination.

In the present invention, the lubricating oil composition for refrigeration machine may further contain oiliness improvers, anti-foaming agents, anti-corrosive agents and colorants, which are generally used for lubricating oils such as refrigeration machine oils, with the proviso that the object of the invention is not marred.

The lubricating oil composition for refrigeration machine according to the invention can be obtained, for example, by adding a specific amount of the fluoroalkyl group-containing alcohol to the specific amount of the carboxylic ester or the carbonic ester, followed by stirring.

The liquid temperature in the stirring is preferably in the range of room temperature to 150 °C. The stirring is carried out preferably in an inert gas atmosphere.

EFFECT OF THE INVENTION

As described above, according to the invention, the lubricating oil composition for refrigeration machine comprises 100 parts by weight of a carboxylic ester having a number-average molecular weight (Mn) of 200 to 5,000 and a kinematic viscosity at 100 °C of 2 to 100 cSt or a carbonic ester having a number-average molecular weight (Mn) of 200 to 5,000 and a kinematic viscosity at 100 °C of 2 to 100 cSt, and 0.001 to 15 parts by weight of a fluoroalkyl group-containing alcohol. Therefore, this composition can prominently reduce the amount of metal abrasion at the slide part of the compression type refrigeration machine in which hydrogenated fluorocarbon such as R-134a is used as a refrigerant.

Further, the lubricating oil composition according to the invention can be also used for refrigeration machines of other types than the compression type because of its excellent lubricating properties.

EXAMPLE

The present invention will be further described with reference to the following examples, but it should be construed that the invention is in no way limited to those examples.

In the examples, the tests for various properties were carried out in accordance with the following methods.

[Test method]

a. Kinematic viscosity at 100 °C and 40 °C and viscosity index

This test was carried out in accordance with JIS K-2283.

b. Density

This test was carried out in accordance with JIS K-2249.

c. Pour point

This test was carried out in accordance with JIS K-2265.

d. Load bearing capacity (Falex value)

After a 5-minute warming-up operation under a load of 250 lbf using a falex tester, the load was increased continuously, and a value of the increased load obtained, at which burn mark appeared, was taken as a value of load bearing capacity, in accordance with ASTM D-2670.

e. Electrical resistance

This test was carried out in accordance with JIS C-2101.

f. Total acid value

This test was carried out in accordance with JIS K-2501.

g. Compatibility with R-134a

The lubricating oil composition and R-134a were introduced in various proportions between them into a glass tube, which was then sealed up, and the composition and R-134a were made compatible with each other to examine the highest and the lowest temperatures (critical temperatures) between which they were compatible with each other, in accordance with JIS K-2211.

h. Amount of abrasion

The abrasion test was carried out using a Falex tester under the following conditions, and the amount of abrasion was determined as loss in weight of a test piece (V block, journal) after subjected to the abrasion test.

Test conditions:

Amount of sample oil: 90 ml
Test piece: V block of A4032 (equivalent to alloy No. 4032 of JIS H4140) and journal standardized in ASTM D-3233
Temperature: 125 °C
Number of revolutions: 260 rpm
Load: 250 lbf for 30 minutes
Type and flow rate of gas (refrigerant): R-134a, 5 l/hr

Reference Example 1

A 5-liter flask equipped with a distillation column of a 10-sieve tray was charged with 588 g (4.98 mol) of 3-methyl-1,5-pentanediol, 2,500 g (21.42 mol) of methylhexanol (a mixture of 87 % of 3-methylhexanol and 13 % of 5-methylhexanol), 1,932 g (21.45 mol) of dimethyl carbonate and 3.8 g (0.020 mol) of a 28 % by weight of methanol solution of $NaOCH_3$.

The mixture was heated at a temperature of 110 to 160 °C for 8 hours under atmospheric pressure to distill off the resulting methanol. The yield of the methanol was 98 %.

Then, the mixture was heated at a temperature of 130 to 170 °C for 8 hours under a reduced pressure (130 to 10 mmHg) to distill off methanol, dimethyl carbonate, methylhexanol and methyl methylhexyl carbonate.

After washing the thus obtained mixture with an aqueous solution containing ammonium carbonate in an amount of 5 times the molar quantity of the $NaOCH_3$ used, an excess di(methylhexyl)carbonate was removed by distillation to obtain 1,480 g of polycarbonate.

As a result of analysis, it was found that the polycarbonate thus obtained is a mixture of dicarbonate having the following structure and its condensate.

$C_7H_{15}OCOOCH_2CH_2CH(CH_3)CH_2CH_2OCOOC_7H_{15}$

The dicarbonate obtained had a number-average molecular weight (Mn), as determined by GPC, of 450, a density of 1.001 g/ml, a kinematic viscosity at 100 °C of 5.67 cSt, a kinematic viscosity at 40 °C of 29.6 cSt and a total acid value of 0.01 mg-KOH/g.

Reference Example 2

[Preparation of carboxylic ester]

A 1-liter four-necked separable flask equipped with a stirring rod, a nitrogen blowing pipe made of glass, a thermometer and a water separator having a cooling tube was charged with 134 g (1.0 mol) of trimethylolpropane, 664 g (4.2 mol) of 3,5,5-trimethylcaproic acid and 2 g of p-toluenesulfonic acid to perform esterification reaction at 190 °C for 8 hours in a stream of nitrogen while removing the resulting water from the system.

After the reaction was completed, the reaction product was washed three times with 250 cc of a 10 % aqueous solution of sodium carbonate, and then dried at 120 °C and 1 Torr for 1 hour under a reduced pressure to obtain 540 g of a 3,5,5-trimethylcaproic acid triester of trimethylolpropane.

The carboxylic ester thus obtained had a number-average molecular weight (Mn), as determined by GPC, of 550, a density of 0.941 g/ml, a kinematic viscosity at 100 °C of 7.1 cSt, a kinematic viscosity at 40 °C of 51.7 cSt and a total acid value of 0.01 mg-KOH/g.

Example 1

100 Parts by weight of the dicarbonate obtained in Reference Example 1 and 4 parts by weight of 2-(perfluorooctyl)ethanol were mixed with each other at 80 °C to give a solution.

The lubricating oil composition thus obtained was subjected to the abrasion test to determine the amount of metal abrasion.

The result is shown in Table 1.

This lubricating oil composition had a kinematic viscosity at 100 °C of 6.0 cSt, a kinematic viscosity at 40 °C of 32.0 cSt, a viscosity index of 136, a pour point of -60.0 °C, a load bearing capacity (Falex value) of 880 lbf, an electrical resistivity of 3.3×10^{15} Ω•cm and a total acid value of 0.01 mg-KOH/g.

Further, the compatibility of the lubricating oil composition with R-134a was evaluated. As a result, it was found that when a weight ratio between the lubricating oil composition and R-134a was 15 : 85, the critical temperature on the higher side was 91 °C, while the critical temperature on the lower side was -60 °C, and the lubricating oil composition was excellent in compatibility with R-134a.

Example 2

The procedure of Example 1 was repeated except that the addition amount of 2-(perfluorooctyl)ethanol was changed to 0.4 part by weight, to obtain a lubricating oil composition.

The lubricating oil composition thus obtained was subjected to the abrasion test to determine the amount of metal abrasion.

The result is shown in Table 1.

Example 3

The procedure of Example 1 was repeated except that 1H,2H,5H-octafluoropentanol was used in place of 2-(perfluorooctyl)ethanol, to obtain a lubricating oil composition.

The lubricating oil composition thus obtained was subjected to the abrasion test to determine the amount of metal abrasion.

The result is shown in Table 1.

Example 4

The procedure of Example 3 was repeated except that the addition amount of 1H,2H,5H-octafluoropentanol was changed to 0.04 part by weight, to obtain a lubricating oil composition.

The lubricating oil composition thus obtained was subjected to the abrasion test to determine the amount of metal abrasion.

The result is shown in Table 1.

Example 5

The procedure of Example 1 was repeated except that the addition amount of 2-(perfluorooctyl)ethanol was changed to 6 parts by weight, to obtain a lubricating oil composition.

The lubricating oil composition thus obtained was subjected to the abrasion test to determine the amount of metal abrasion.

The result is shown in Table 1.

Example 6

The procedure of Example 1 was repeated except that the carboxylic ester of Reference Example 2 was used in place of the dicarbonate of Reference Example 1, to obtain a lubricating oil composition.

The lubricating oil composition thus obtained was subjected to the abrasion test to determine the amount of metal abrasion.

The result is shown in Table 1.

Comparative Example 1

Only the dicarbonate of Reference Example 1 was subjected to the abrasion test to determine the amount of metal abrasion.

The result is shown in Table 1.

Comparative Example 2

The procedure of Example 1 was repeated except that the addition amount of 2-(perfluorooctyl)ethanol was changed to 0.0004 part by weight, to obtain a lubricating oil composition.

The lubricating oil composition thus obtained was subjected to the abrasion test to determine the amount of metal abrasion.

The result is shown in Table 1.

Comparative Example 3

Only the carboxylic ester of Reference Example 2 was subjected to the abrasion test to determine the amount of metal abrasion.

The result is shown in Table 1.

Table 1

	Lubricating oil base		Fluoroalkyl group-containing alcohol		Amount of abrasion [mg]		
	Type	Amount	Type	Amount	V block	Journal	Total
Ex.1	Carbonic ester of Ref.Ex.1	100	A	4	0	1	1
Ex.2	Carbonic ester of Ref.Ex.1	100	A	0.4	1	9	10
Ex.3	Carbonic ester of Ref.Ex.1	100	B	4	1	1	2
Ex.4	Carbonic ester of Ref.Ex.1	100	B	0.04	1	11	12
Ex.5	Carbonic ester of Ref.Ex.1	100	A	6	1	2	3
Ex.6	Carboxylic ester of Ref.Ex.2	100	A	4	2	10	12
Comp. Ex.1	Carbonic ester of Ref.Ex.1	100	-	-	4	15	19
comp. Ex.2	Carbonic ester of Ref.Ex.1	100	A	0.0004	4	14	18
Comp. Ex.3	Carboxylic ester of Ref.Ex.2	100	-	-	7	20	27

Remarks:
1. The unit of each amount of the carbonic ester, the carboxylic ester and the fluoroalkyl group-containing alcohol is part(s) by weight.
2) Type of the fluoroalkyl group-containing alcohol
A: 2-(perfluorooctyl)ethanol
B: 1H,2H,5H-octafluoropentanol

Claims

1. A lubricating oil composition for refrigeration machine comprising:

100 parts by weight of a carboxylic ester having a number-average molecular weight (Mn) of 200 to 5,000 and a kinematic viscosity at 100 °C of 2 to 100 cSt or a carbonic ester having a number-average molecular weight (Mn) of 200 to 5,000 and a kinematic viscosity at 100 °C of 2 to 100 cSt, and

0.001 to 15 parts by weight of a fluoroalkyl group-containing alcohol.

2. The lubricating oil composition for refrigeration machine as claimed in claim 1, wherein the fluoroalkyl group-containing alcohol has a molecular weight of 30 to 2,000.

3. The lubricating oil composition for refrigeration machine as claimed in claim 1 or 2, wherein said composition is used for compression type refrigeration machine.

4. The lubricating oil composition for refrigeration machine as claimed in claim 3, wherein said composition is used for compression type refrigeration machine in which a hydrogenated fluorocarbon (HFC) is used as a refrigerant.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 11 8009

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
Y	WO-A-92 08774 (ALLIED SIGNAL INC.) * page 12, line 1 - line 8 * * page 12, line 10 - line 18 * * page 26; examples 8-15 * * page 28; example 60 * * page 28, line 14 * * claims 2,11 * ---	1-4	C10M169/04 C10M171/00 //(C10M169/04, 105:32,105:48, 131:10), C10N20:02, C10N20:04, C10N30:06, C10N40:30
Y	EP-A-0 428 757 (IDEMITSU KOSAN COMPANY LIMITED) * page 5, line 50 - line 51; table 1 * ---	1-4	
A	DATABASE WPI Section Ch, Week 9006, Derwent Publications Ltd., London, GB; Class E16, AN 90-041701 & JP-A-1 319 589 (MATSUSHITA ELEC IND KK) 25 December 1989 * abstract * ---	1-4	
A	DATABASE WPI Section Ch, Week 8804, Derwent Publications Ltd., London, GB; Class A97, AN 88-026403 & JP-A-62 288 692 (HITACHI KK) 15 December 1987 * abstract * ---	1-4	TECHNICAL FIELDS SEARCHED (Int.Cl.6) C10M
A	EP-A-0 514 988 (SHELL INTERNATIONAL RESEARCH MAATSCHAPPIJ) * page 4, line 22 - line 23 * * page 4, line 40 * ---	1,3,4	
A	EP-A-0 550 407 (NIPPON OIL CO.) * page 10, line 41 - line 58 * * page 11; example 1 * * page 14; example 1 * --- -/--	1,3,4	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	15 March 1995	Hilgenga, K

CATEGORY OF CITED DOCUMENTS

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	WO-A-93 19142 (THE BRITISH PETROLEUM COMPANY) * page 2, line 12 - line 13 * * page 3, line 5 - line 7 * * page 4, line 9 - line 11 * ---		
A	US-A-5 002 678 (A.R. VANOVER) * column 5, line 30; claims 1,2 * -----		

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

The present search report has been drawn up for all claims

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