(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 3 305 878 A1

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 153(4) EPC

(43) Date of publication:
11.04.2018 Bulletin 2018/15

(21) Application number: **16807425.0**

(22) Date of filing: **06.06.2016**

(51) Int Cl.:
C10M 105/42 $^{(2006.01)}$
C10N 20/00 $^{(2006.01)}$
C10N 30/06 $^{(2006.01)}$
C10N 30/08 $^{(2006.01)}$
C10N 40/30 $^{(2006.01)}$

(86) International application number:
PCT/JP2016/066756

(87) International publication number:
WO 2016/199718 (15.12.2016 Gazette 2016/50)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
MA MD

(30) Priority: **08.06.2015 JP 2015115892**

(71) Applicant: **NOF Corporation**
Shibuya-ku
Tokyo 150-6019 (JP)

(72) Inventors:
- **YOSHIKAWA fumitaka**
  Amagasaki-shi
  Hyogo 660-0095 (JP)
- **KAJIKI Takeshi**
  Amagasaki-shi
  Hyogo 660-0095 (JP)
- **YAMADA Munehiro**
  Amagasaki-shi
  Hyogo 660-0095 (JP)
- **UEDA Seita**
  Amagasaki-shi
  Hyogo 660-0095 (JP)

(74) Representative: **Naylor, Matthew John et al**
Mewburn Ellis LLP
City Tower
40 Basinghall Street
London EC2V 5DE (GB)

(54) ESTER FOR REFRIGERATION OIL AND WORKING FLUID COMPOSITION FOR REFRIGERATION OIL

(57) An ester for a refrigerator oil is obtained from the following components (A), (B), (C) and (D). The ester contains a unit derived from the component (B) in a ratio of 0.1 to 0.4 mole, a unit derived from the component (C) in a ratio of 0.8 to 2.8 mole and a unit derived from the component (D) in a ratio of 0.3 to 2,3 mole with respect to 1.0 mole of a unit derived from said component (A). The ester has a hydroxyl value of 5 to 40 mgKOH/g and satisfies the formulas (1) and (2). (A) neopentyl glycol; (B) a linear dihydric alcohol having 2 to 6 carbon atoms including carbons at both terminals and hydroxyl groups connected to the carbons at both terminals, respectively; (C) a linear dicarboxylic acid having 4 to 10 carbon atoms including carbons at both terminals and carboxyl groups connected to the carbons at both terminals, respectively; (D) a monohydric alcohol having 6 to 12 carbon atoms; $0.08 \leqq B_{OH}/(A_{OH}+B_{OH}) \leqq 0.15$ ···(1); $[B_{OH}/(A_{OH}+B_{OH})]/[B_{mol}/(A_{mol}+B_{mol})] \leqq 0.9$ ... (2); (A_{OH} represents a molar number of terminal hydroxyl groups derived from the component (A); B_{OH} represents a molar number of terminal hydroxyl groups derived from the component (B); A_{mol} represents a molar number of the unit derived from said component (A); and B_{mol} represents a molar number of the unit derived from the component (B))]

EP 3 305 878 A1

Printed by Jouve, 75001 PARIS (FR)

Description

(Technical field)

[0001] The present invention relates to an ester for a refrigerator oil having excellent lubricating and heat resistant properties. Further, it relates to an ester for a refrigerator oil, which is used for a working fluid composition for an refrigerator oil containing a non-chlorine-based Freon refrigerant or natural refrigerant.

BACKGROUND ARTS

[0002] In a air conditioning apparatuses such as a room air conditioner and packaged air conditioner, a low temperature apparatus such as a refrigerating and freezing machine for home use, a freezer for industrial use, and a car air conditioner for a hybrid car, electric car or the like, instead of a Freon refrigerant containing chlorine causing destruction of ozone layer, it has been used a hydrofluorocarbon (HFC) refrigerant such as 1,1,1,2-tetrafluoroethane (R-134a), pentafluoroethane (R-125), and a refrigerant mixture (R-410A) of difluoromethane (R-32) and R-125 or the like.

[0003] However, although the Ozone Depletion Potentials of the HFC refrigerants as described above are zero, the Global Warming Potentials (GWP) of them are as high as 1000 or higher. These refrigerants are thus subjected to regulations targeting reduction of greenhouse effect, and the applications are limited. It has been thus studied the use of a refrigerant having a lower GWP. For example, it has been proceeded the conversion to the single use of 2,3,3,3-tetrafluoropropene (HFO-1234yf) with a GWP of 4 or R-32 with a GRP of 67 singly.

[0004] As the conversion to the HFC refrigerant of a low GWP is proceeded, it has been proposed various kinds of esters for a refrigerator oil using, as a base oil, a polyol ester whose compatibility with the low GWP refrigerant is high. Further, among the alternative candidates of the refrigerants, in the case that R-32 or refrigerant mixture containing R-32 is used, the pressure of the refrigerant is elevated and the discharge temperature at a compressor is high in use, so that the lubricating condition in the compressor becomes more severe. It has been thus proposed an ester for a refrigerator oil whose lubricating property and stability are improved.

[0005] For example, according to patent document 1, responsive to the use of the refrigerant mixture containing R-32, as a ester having high stability in the compressor driven under the thermally severe condition, it is disclosed a lubricating oil for a refrigerator oil containing, as its main component, an ester composed of pentaerythritol, 2-ethylhexanoic acid and 3,5,5-trimethylhexanoic acid.

[0006] Further, in the case of hydrocarbon (HC) refrigerants, the molecule of HC does not have fluorine atoms improving the lubricating property so that the improvement of the lubricating property is not expected, different from the HFC refrigerants. Further, the solubility of the refrigerator oil to the HC refrigerants is high to lower the viscosity of the oil, so that the lubricating condition becomes more severe. According to patent document 2, it is proposed a complex ester having excellent lubricating and heat resistant properties under such severe lubrication condition. It is further disclosed that the lubricating property can be improved by using 1,4-butanediol and the heat resistant property can be improved by using a monohydric alcohol as raw materials.

Prior art documents

(Patent documents)

[0007]

(Patent document 1) Japanese Patent Publication No. 10-008084A
(Patent document 2) WO 2014/017596 B1

SUMMARY OF THE INVENTION

(Object to be solved by the invention)

[0008] However, as the compactification (reduction of used amount of a refrigerator oil per one apparatus) and energy saving (extension of operation time of a compressor by inverter control) of an apparatus using the refrigerator oil is proceeded, the condition of use of the refrigerator oil becomes more severe. As a result, due to friction heat generated at sliding parts of the compressor, the refrigerator oil is subjected to local high temperature condition and thereby decomposed, so that the thus generated decomposition products would possibly corrode metal parts and adversely affect a resin material. It is thus demanded the development of an ester for the refrigerator oil providing excellent lubricating property and thermal stability under more severe condition.

[0009] An object of the present invention is to provide an ester lubricant oil for a refrigerator oil having excellent lubricating and heat resistant properties.

(Solution for the object)

[0010] As the inventors have intensively studied for solving the above problems, it is found that excellent lubricant and heat resisting properties can be attained by an ester containing a specific dihydric alcohol, dicarboxylic acid and monohydric alcohol. The invention was thus made.

[0011] That is, the present invention provides the followings.

(1) An ester for a refrigerator oil, said ester being obtained from the following component (A), component (B), component (C) and component (D):

wherein said ester comprises a unit derived from said component (B) in a ratio of 0.1 to 0.4 mole, a unit derived from said component (C) in a ratio of 0.8 to 2.8 mole and a unit derived from said component (D) in a ratio of 0.3 to 2,3 mole with respect to 1.0 mole of a unit derived from said component (A):
wherein said ester has a hydroxyl value of 5 to 40 mgKOH/g; and
wherein said ester satisfies the following formulas (1) and (2).

(A) neopentyl glycol
(B) a linear dihydric alcohol having 2 to 6 carbon atoms including carbons at both terminals and hydroxyl groups connected to said carbons at said both terminals, respectively
(C) a linear dicarboxylic acid having 4 to 10 carbon atoms including carbons at both terminals and carboxyl groups connected to said carbons at said both terminals, respectively
(D) a monohydric alcohol having 6 to 12 carbon atoms

$$0.08 \leqq B_{OH}/(A_{OH}+B_{OH}) \leqq 0.15 \quad \cdots (1)$$

$$[B_{OH}/(A_{OH}+B_{OH})] \;/\; [B_{mol}/(A_{mol}+B_{mol})] \leqq 0.9 \quad \cdots (2)$$

(In said formulas (1) and (2),

A_{OH} represents a molar number of terminal hydroxyl groups derived from said component (A) in said ester;
B_{OH} represents a molar number of terminal hydroxyl groups derived from said component (B) in said ester;
A_{mol} represents a molar number of said unit derived from said component (A) in said ester; and
B_{mol} represents a molar number of said unit derived from said component (B) in said ester.)

(2) A working fluid composition for a refrigerator oil, said fluid composition comprising a non-chlorine-based Freon refrigerant or a natural refrigerant, and said ester for said refrigerator oil.

[0012] Further, for obtaining the ester for a refrigerator oil, preferably, the component (A), component (B), component (C) and component (D) are subjected to a first esterification at a temperature of 100 to 150°C and then subjected to a second esterification at a temperature of 150 to 250°C.

EFFECTS OF THE INVENTION

[0013] As the ester for the refrigerator oil of the present invention has high heat resistant property, it can be appropriately used for a compressor of a freezing and air-conditioning apparatus, particularly requiring thermal stability. Further, as the ester for the refrigerator oil of the present invention has high compatibility with a non-chlorine-based Freon refrigerant or a natural refrigerant, it can be appropriately used for a working fluid composition for a refrigerator containing such refrigerant.

EMBODIMENTS FOR CARRYING OUT THE INVENTION

[0014] The ester for the refrigerator oil of the present invention will be described below.

[0015] Further, numerical ranges defined by using a sign "-" in the specification, the numerical range is to contain numerical values at both ends (upper limit and lower limit) of "-". For example, "2 - 5" means "not less than 2 and not more than 5".

[0016] The ester for the refrigerator oil of the present invention is obtained by the mixing and esterification of neopentyl glycol (component (A)), a linear dihydric alcohol having 2 to 6 carbon atoms including carbons at both terminals and hydroxyl groups connected to said carbons at said both terminals, respectively (component (B)), a linear dicarboxylic acid having 4 to 10 carbon atoms including carbons at both terminals and carboxyl groups connected to said carbons at said both terminals, respectively (component (C)) and a monohydric alcohol having 6 to 12 carbon atoms (component (D)).

[0017] Further, the terms representing the components (A), (B), (C) and (D) are general names for convenience sake, and one compound or plural compounds may be included in each of the components. In the case that two or more kinds of compounds are included in each of the components, the ratio of the component is defined as a total value of the ratios of the two or more kinds of the compounds belonging to the component.

[0018] As neopentyl glycol used as the component (A) in the present invention, it may be used neopentyl glycol available in the industry. As to the state of neopentyl glycol, it may be used solid or liquid state diluted with water.

[0019] The component (B) is the linear dihydric alcohol having 2 to 6 carbon atoms including carbons at both terminals and hydroxyl groups connected to the carbons at both terminals, respectively. Specifically, it includes ethylene glycol, 1, 3-propane diol, 1,4-butane diol, 1,5-pentane diol, 1, 6-haxane diol and the like. It may preferably be a linear, dihydric saturated alcohol and particularly preferably be 1,4-butane diol. By using the component (B), it can be obtained the ester excellent in viscosity index, stability at low temperature and lubricating property.

[0020] The component (C) is the linear dicarboxylic acid having 4 to 10 carbon atoms including carbons at both terminals and carboxyl groups connected to the carbons at both terminals, respectively. Specifically, it includes succinic acid (carbon number of 4), glutaric acid (carbon number of 5), adipic acid (carbon number of 6), pimelic acid (carbon number of 7), suberic acid (carbon number of 8), azelaic acid (carbon number of 9), sebacic acid (carbon number of 10) and the like. It is preferably used a linear saturated dicarboxylic acid having a carbon number of 6 to 8. By using the component (C), it can be obtained the ester excellent in the viscosity index and stability at low temperature.

[0021] The component (D) is the monohydric alcohol having 6 to 12 carbon atoms, which may be a linear or branched alcohol. Specifically, it includes 1-haxanol, 1-heptanol, 1-octanol, 1-nonanol, 1-decanol, 1-undecanol, 1-dodecanol, 2-ethylhexanol, 3,5,5-trymethylhexanol and the like. It may preferably be a linear branched alcohol having a carbon number of 6 to 10, so that it can be obtained the ester excellent in stability at low temperature. It is particularly preferred to use 2-ethylhexanol or 3,5,5-trimethylhexanol.

[0022] The ester for the refrigerator oil of the present invention is composed of a unit derived from the component (B) in a ratio of 0.1 to 0.4 mole, a unit derived from the component (C) in a ratio of 0.8 to 2.8 mole and a unit derived from the component (D) in a ratio of 0.3 to 2.3 mole with respect to 1.0 mole of a unit derived from the component (A).

[0023] In the case that the amount of the unit derived from the component (B) is lower than 0.1 mole with respect to 1.0 mole of the unit derived from the component (A), desired viscosity index and lubricating property are hard to obtain. In the case that it exceeds 0.4 mole, the stability at low temperature of the ester is deteriorated. The amount of the unit derived from the component (B) may preferably be 0.1 to 0.3 mole, with respect to 1.0 mole of the unit derived from the component (A).

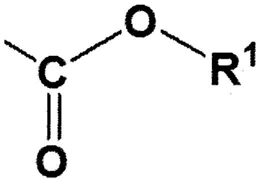
[0024] In the case that the amount of the unit derived from the component (C) is lower than 0.8 mole with respect to 1.0 mole of the unit derived from the component (A), a high viscosity index is hard to attain. In the case that it exceeds 2.8, the lubricating property is hard to obtain. The amount of the unit derived from the component (C) may preferably be 0.9 mole or higher and preferably be 2.3 mole or lower, with respect to 1.0 mole of the unit derived from the component (A).

[0025] In the case that the amount of the unit derived from the component (D) is made 0.3 to 2.3 mole with respect to 1.0 mole of the unit derived from the component (A), it is easily obtained the ester whose viscosity is appropriate as a refrigerator oil. The amount of the unit derived from the component (D) may preferably be 0.5 mole or higher and preferably be 2.1 mole or lower, with respect to 1.0 mole of the unit derived from the component (A).

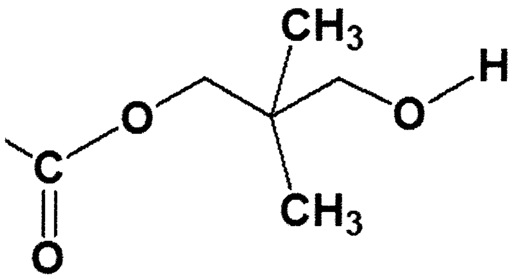
[0026] The molar ratios of the respective units described above are calculated by analysis with a gas chromatography. 0.1 g of each ester is diluted with 5 g of solvent mixture of toluene/methanol (80 weight percent/ 20 weight percent), and 0.3 g of 28% sodium ethoxide methanol solution (Wako Pure Chemical Industries Ltd.) is added thereto, followed by standing at 60°C for 30 minutes so that the ester is subjected to methanolysis. The solution obtained by the methanolysis of the ester is analyzed by using the gas chromatography to obtain ratios of areas of peaks corresponding with the components (A), (B), (C) and (D), respectively. The ratios of the areas are converted to molar ratios to calculate them. Further, each of the components is analyzed by the gas chromatography so that the components contained in the product of the methanolysis can be identified.

[0027] According to the synthesized ester of the present invention, the molar ratios of the units derived from the respective components (A), (B), (C) and (D) are adjusted so that the carboxyl groups of the component (C) are terminated by the component (A), (B) or (D). It is contained, in the ester, an ester whose terminal structure is composed of alkyl groups derived from the component (D), as well as esters whose terminal structures are composed of hydroxyl groups derived from the component (A) and hydroxyl groups derived from the component (B), respectively as minor components.

[0028] Examples of specific terminal structures of the ester of the present invention will be described referring to formulas (3), (4) and (5). The formula (3) shows the structure having the alkyl group derived from the component (D) at the terminal of the ester, the formula (4) shows the structure having hydroxyl group derived from the component (A) at the terminal of the ester, and the formula (5) shows the structure having hydroxyl group derived from the component (B) at the terminal of the ester.

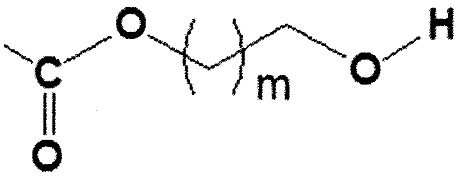


(3)



,

(4)



(5)

m represents an integer of 1 to 5, and R^1 represents an alkyl group derived from the component, (D).

[0029] Such design of structure is applied so that it is possible to provide the ester hard to hydrolyze or decompose thermally and excellent in stability in using as a refrigerator oil.

[0030] The ester for the refrigerator oil of the present invention satisfies the following formulas (1) and (2).

$$0.08 \leqq B_{OH}/(A_{OH}+B_{OH}) \leqq 0.15 \quad \cdots (1)$$

(A_{OH} represents a molar number of terminal hydroxyl groups derived from the component (A) in the ester; and B_{OH} represents a molar number of terminal hydroxyl groups derived from the component (B) in the ester.)

[0031] The formula (1) means the molar ratio of the terminal hydroxyl groups derived from the component (B) with respect to a total of those of the terminal hydroxyl groups derived from the component (A) and terminal hydroxyl groups derived from the component (B) in the ester.

$$[B_{OH}/(A_{OH}+B_{OH})] / [B_{mol}/(A_{mol}+B_{mol})] \leqq 0.9 \cdots(2)$$

(A_{OH} represents a molar number of terminal hydroxyl groups derived from the component (A) in the ester;
B_{OH} represents a molar number of terminal hydroxyl groups derived from the component (B) in the ester;
A_{mol} represents a molar number of the unit derived from the component (A) in the ester; and
B_{mol} represents a molar number of the unit derived from the component (B) in the ester.)

[0032] The fraction of the formula (2) is $[B_{OH}/(A_{OH}+B_{OH})]$, which is shown in the formula (1), and means the molar ratio of the terminal hydroxyl groups derived from the component (B) with respect to a total of those of the terminal hydroxyl groups derived from the component (A) and terminal hydroxyl groups derived from the component (B) in the ester.

[0033] On the other hand, the denominator of the formula (2) is $[B_{mol}/(A_{mol}+B_{mol})]$, which means the molar ratio of the unit derived from the component (B) with respect to a total of those of the unit derived from the component (A) and unit derived from the component (B) in the ester.

[0034] Therefore, the formula (2) indicates the degree of how low the molar ratio of the terminal hydroxyl groups derived from the component (B), with respect to the molar ratio of the unit derived from the component (B)is in the ester. In other words, it means the degree of deviation of the component (B) in the terminal structure with respect to the whole structure of the ester.

[0035] Further, each of the numerical values of the formulas (1) and (2) is measured as described below.

(Numerical value of the formula (1) and fraction of the formula (2) $[B_{OH}/(A_{OH}+B_{OH})]$)

[0036] Based on ^{1}H-NMR spectrum, it is calculated an integrated value of a peak (3.2 to 3.4 ppm) corresponding to α-hydrogen of the hydroxyl groups derived from the component (A) and an integrated value of a peak (3.6 to 3.8 ppm) of α-hydrogen of the hydroxyl groups derived from the component (A). The integrated value of the α-hydrogen of the hydroxyl groups derived from the component (B) is divided by a total of the respective integrated values to calculate the numerical values.

[0037] (Numerical value of denominator of formula (2):

$$[B_{mol}/(A_{mol}+B_{mol})])$$

[0038] The molar numbers of the units derived from the components (A) and (B) are obtained based on the gas chromatography analysis described above to calculate the molar ratios.

[0039] As hydrogen atom is not bonded to the β-carbon (B-hydrogen is not included) in the component (A), as to the terminal hydroxyl group generated at the terminal of the ester structure, the terminal structure derived from the component (A) is excellent in the heat resistant property with respect to that derived from the component (B). That is, the ester, in which the ester terminal structure derived from the component (A) is predominant, is superior in heat resistant property than an ester in which the ester terminal structure derived from the component (A) is not predominant. As a result, by lowering the molar ratio of the hydroxyl group derived from the component (B) with respect to the total of those of the hydroxyl groups to 0.15 or lower, it is possible to provide the ester having more excellent heat resistance. In the case that the molar ratio of the terminal hydroxyl groups derived from the component (B) with respect to the total of those of the terminal hydroxyl groups derived from the component (A) and the terminal hydroxyl groups derived from the component (B) is 0.08 to 0.15, it is easier to obtain the ester excellent in the lubricating and heat resistant properties. On the viewpoint, the molar ratio may more preferably be 0.09 or higher, and more preferably be 0.14 or lower.

[0040] Further, according to the ester in which the molar ratio of the terminal hydroxyl groups derived from the component (B) with respect to the molar ratio of the unit derived from the component (B) is deviated and made lower in the ester, the heat resistant property can be made more excellent. The degree of the deviation of the component (B) in the terminal structure can be indicated by the molar ratio of the terminal hydroxyl groups derived from the component (B) with respect to the molar ratio of the unit derived from the component (B) in the ester. By making the value at 0.9 or lower, it is possible to obtain the ester having improved heat resistant property. The value is made 0.9 or lower and more preferably be made 0.8 or lower. Although the lower limit is not particularly defined, the value may preferably be 0.2 or higher, more preferably be 0.3 or higher and most preferably be 0.5 or higher.

[0041] According to the ester of the present invention, the molar ratio of the hydroxyl groups derived from the component

(B) with respect to the total of the hydroxyl groups in the ester is lowered, with respect to the molar ratio of the unit derived from the component (B) to the total of the units derived from the component (A) and the component (B) in the ester. According to the reason as described above, the ester satisfying the formulas (1) and (2) provides the ester more excellent in the heat resistant property.

[0042] As to the production of the ester, the above components (A), (B), (C) and (D) are charged in an appropriate reactor first, and subjected to esterification at ambient pressure under nitrogen atmosphere. The esterification may be normally performed at 150 to 250 °C for removing water generated during the reaction effectively. However, on the viewpoint of obtaining the ester having more excellent heat resistant property, a first esterification is performed at 100 to 150°C, and a second esterification is then performed at 150 to 250°C.

[0043] The first esterification may be performed preferably at 100 to 140°C and more preferably at 100 to 130°C, so that the ester excellent in the heat resistant property can be easily obtained. Further, the first esterification may be performed preferably for 1 to 10 hours and more preferably for 2 to 8 hours, so that the ester excellent in the heat resistant property can be easily obtained.

[0044] The second esterification may be performed preferably at 160 to 260°C and more preferably at 180 to 250°C. At this time, the second esterification is performed until the acid value reaches 10 mgKOH/g or lower, preferably 5 mgKOH/g or lower, and most preferably 2 mgKOH/g or lower.

[0045] Further, although the esterification may be performed using a Bronsted acid catalyst or Lewis acid catalyst, it may be preferably performed without using a catalyst.

[0046] After the esterification, excessive amount of the component (D) is evaporated under a low pressure to obtain crude ester. The crude ester is then subjected to purification treatment using an adsorbent to obtain the target ester for a refrigerator oil.

[0047] The kinematic viscosity at 40°C of the ester for the refrigerator oil of the present invention is preferably 20 to 500 mm^2/s, more preferably 20 to 300 mm^2/s, still more preferably 20 to 250 mm^2/s, and most preferably 20 to 180 mm^2/s. Further, the hydroxyl value may preferably be 5 to 40 mgKOH/g and more preferably be 15 to 35 mgKOH/g.

[0048] The ester for the refrigerator oil of the present invention may be used alone as a base oil or may be used after mixing with another base oil. Further, it may be added thereto a known additive such as a phenolic antioxidant, metal deactivator including benzotriazole, tiazole or dithiocarbamate, an acid scavenger including an epoxy compound or carbodiimide, and phosphorous-based extreme pressure agent, depending on the intended use.

[0049] As the ester for the refrigerator oil of the present invention has good solubility with a non-chlorine-type Freon refrigerant or natural refrigerant, it can be preferably used for a fluid composition for a refrigerator containing such refrigerant. It may be used a pure material or the mixture thereof of the non-chlorine type Freon refrigerant including hydrofluorocarbon (HFC), hydrofluoro olefin (HFO), hydrocarbon (HC) or a natural coolant.

[0050] Specific examples of the hydrofluorocarbon (HFC) include either one or the mixture of two or more of 1,1,1,2-tetrafluoroethane (R-134a), pentafluoroethane (R-125), difluoroethane (R-32), trifluoroethane(R-23), 1,1,2,2-tetrafluoroethane (R-134), 1,1,1-trifluoroethane (R-143a), 1,1-difluoroethane (R-152a) and the like. The mixed refrigerant includes, for example, R-407C (R-134a/R-125/R-32 = 52/25/23 weight%), R-410R (R-125/R-32 = 50/50 weight%), R-404A (R-125/R-143/R-134a = 44/52/4 weight %), R-407E (R-134a/R-125/R-32 = 60/15/25 weight %), R-410B(R-32/R-125 = 45/55 weight %) and the like. Among them, it is preferred a refrigerant containing at least one of R-134a and R-32, and a single kind refrigerant of R-32 is more preferred.

[0051] Specific examples of the hydrofluorocarbon refrigerants include either one or the mixtures thereof 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), 3,3,3-trifluoropropene (HFO-1243zf) and the like. On the viewpoint of the refrigeration property, it is preferred one or two or more selected from (HFO-1225ye), (HFO-1234ze) and (HFO-1234yf).

[0052] Further, the hydrocarbon (HC) refrigerant includes propane (R290), isobutene (R600a) or the like and the mixture thereof. The natural refrigerator includes ammonia, carbon dioxide and the like. R290, R600 and carbon dioxide are particularly preferred.

[0053] According to the fluid composition for the refrigerator oil, usually, the ratio of the masses of the ester for the refrigerator oil of the present invention and the non-chlorine-based Freon refrigerant or natural refrigerant is 10:90 to 90:10. In the case that the ratio of the mass of the refrigerant is within this range, the working fluid composition has an appropriate viscosity, so that the lubricating property is excellent and the refrigeration efficiency is high, which is preferred.

EXAMPLES

[0054] Although the examples of the present invention will be described further in detail below, the present invention is not to be restricted to the following examples.

[0055] Further, various kinds of the esters for the refrigerator oil obtained in the inventive and comparative examples are analyzed according to the following methods.

Acid value is measured according to JIS K2501.
Hydroxyl value is measured according to JIS K0070.
Kinematic viscosity is measured according to JIS K2283.

(Production in Example 1)

[0056] 124g (1.19mol) of neopentyl glycol, 30g (0.34mol) of 1,4-butanediol, 355g (2.43mol) of adipic acid and 339g (2.35mol) of 3,5,5-trimethylhexanol were charged into a 4-necked flask and then subjected to reaction under nitrogen atmosphere and ambient pressure at 120 °C for 3 hours while water generated by the reaction was evaporated. Thereafter, the reaction was continued for 7 hours at 200°C until the acid value was lowered to 2 or less. Then, excess amount of 3, 5, 5-trimethylhexanol was evaporated at 200°C under a low pressure of 1 to 5 kPa to obtain crude ester. The crude ester was cooled and subjected to adsorption treatment by adding acid clay and silica-alumina-based adsorbent in amounts of 1.0 weight percent, respectively, of the ester obtained theoretically. The temperature, pressure and time period for the adsorption treatment were made 100 °C, 1 to 5 kPa and 2 hours, respectively. Finally, a filter of 1 micron was used to perform the filtration to obtain target ester.

(Production in Example 2)

[0057] 180g (1.73mol) of neopentyl glycol, 25g (0.28mol) of 1,4-butane diol, 360g (2.47mol) of adipic acid, and 256g (1.78mol) of 3,5,5-trimethylhexanol were charged into a 4-necked flask and then subjected to reaction under nitrogen atmosphere and ambient pressure at 115 °C for 4 hours while water generated by the reaction was evaporated. The subsequent process steps were performed similarly as the Example 1 to obtain target ester.

(Production in Example 3)

[0058] 205g (1.97mol) of neopentyl glycol, 26g (0.28mol) of 1,4-butane diol, 373g (2.55mol) of adipic acid, and 217g (1.50mol) of 3,5,5-trimethylhexanol were charged into a 4-necked flask and then subjected to reaction under nitrogen atmosphere and ambient pressure at 125 °C for 3 hours while water generated by the reaction was evaporated. The subsequent process steps were performed similarly as the Example 1 to obtain target ester.

(Production in Example 4)

[0059] 174g (1.66mol) of neopentyl glycol, 46g (0.51mol) of 1,4-butane diol, 373g (2.55mol) of adipic acid and 238g (1.65mol) of 3,5,5-trimethylhexanol were charged into a 4-necked flask and then subjected to reaction under nitrogen atmosphere and ambient pressure at 120 °C for 4 hours while water generated by the reaction was evaporated. The subsequent process steps were performed similarly as the Example 1 to obtain target ester.

(Production in Example 5)

[0060] 129g (1.23mol) of neopentyl glycol, 28g (0.26mol) of 1,5-pentane diol, 393g (2.25mol) of suberic acid and 300g (2.30mol) of n-octanol were charged into a 4-necked flask and then subjected to reaction under nitrogen atmosphere and ambient pressure at 120 °C for 5 hours while water generated by the reaction was evaporated. The subsequent process steps were performed similarly as the Example 1 to obtain target ester.

(Production in Example 6)

[0061] 215g (2.07mol) of neopentyl glycol, 22g (0.29mol) of 1,3-propane diol, 385g (2.64mol) of adipic acid and 214g (1.49mol) of 3,5,5-trimethylhexanol were charged into a 4-necked flask and then subjected to reaction under nitrogen atmosphere and ambient pressure at 120 °C for 4 hours while water generated by the reaction was evaporated. The subsequent process steps were performed similarly as the Example 1 to obtain target ester.

(Production in Example 7)

[0062] 211g (2.03mol) of neopentyl glycol, 42g (0.36mol) of 1,6-hexane diol, 385g (2.64mol) of adipic acid and 206g (1.43mol) of 3,5,5-trimethylhexanol were charged into a 4-necked flask and then subjected to reaction under nitrogen atmosphere and ambient pressure at 115 °C for 5 hours while water generated by the reaction was evaporated. The subsequent process steps were performed similarly as the Example 1 to obtain target ester.

(Production in Comparative Example 1)

[0063] 174g (1.66mol) of neopentyl glycol, 46g (0.51mol) of 1,4-butane diol, 373g (2.55mol) of adipic acid and 238g (1.65mol) of 3,5,5-trimethylhexanol were charged into a 4-necked flask and then subjected to reaction under nitrogen atmosphere and ambient pressure at 200 °C for 7 hours while water generated by the reaction was evaporated, until the acid value was lowered to 2 or less. Then, excess amount of 3, 5, 5-trimethylhexanol was evaporated at 200°C under a low pressure of 1 to 5 kPa to obtain crude ester. The crude ester was cooled and subjected to adsorption treatment by adding acid clay and silica-alumina-based adsorbent in amounts of 1.0 weight percent, respectively, of the ester obtained theoretically. The temperature, pressure and time period for the adsorption treatment were made 100 °C, 1 to 5 kPa and 2 hours, respectively. Finally, a filter of 1 micron was used to perform the filtration to obtain target ester.

(Production in Comparative Example 2)

[0064] 104g (1.00mol) of neopentyl glycol, 27g (0.30mol) of 1,4-butane diol and 351g (2.40mol) of adipic acid were charged into a 4-necked flask and then subjected to reaction under nitrogen atmosphere and ambient pressure at 200 °C for 3 hours while water generated by the reaction was evaporated, until the acid value was lowered to 270 or less to obtain an intermediate for an ester. 361 g (2.50 mol) of 3, 5, 5-trimethylhexanol was further added to the intermediate for the ester and the reaction was continued for 7 hours until the acid value was lowered to 2 or less. Then, excess amount of 3, 5, 5-trimethylhexanol was evaporated at 200°C under a low pressure of 1 to 5 kPa to obtain crude ester. The crude ester was cooled and subjected to adsorption treatment by adding acid clay and silica-alumina-based adsorbent in amounts of 1.0 weight percent, respectively, of the ester obtained theoretically. The temperature, pressure and time period for the adsorption treatment were made 100 °C, 1 to 5 kPa and 2 hours, respectively. Finally, a filter of 1 micron was used to perform the filtration to obtain target ester.

Heat resistance test (Heating test)

[0065] The ester for the refrigerator oil described above was subjected to heating test to evaluate the heat resistant property of the ester for the refrigerator oil. As to the heat resistant test, the ester was heated under nitrogen atmosphere in a constant temperature bath at 130°C for 72 hours to measure the acid value of the ester for the refrigerator oil after the heating.

Lubricating property (SRV test)

[0066] The ester for the refrigerator oil described above was evaluated in the lubricating property by an SRV testing system. The SRV test was performed using ball/disk and test pieces supplied by "SUJ-2" were used. The test was performed under a testing temperature of 60 °C, a load of 100 N, a magnitude of 1 mm and frequency of 50 Hz. It was measured the wear scar diameter after a testing time of 25 minutes.

[0067] The conditions for the production in the Inventive Examples 1 to 7 and Comparative Examples 1 and 2 were shown in tables 1 and 2, and the physical values, heat resistant and lubricating properties were described in tables 3 and 4. Further, tables 1 and 2 describe the ratios of charging of the respective components, and tables 3 and 4 describes the measured values of the molar ratios of the units derived from the respective components in the thus generated ester.

Table 1

			Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5
First Reaction	Charge (mole) ※ Numeral in parenthesis indicates molar ratio to 1 mole of component (A)	Component (A)	1.19 (1.00)	1.73 (1.00)	1.97 (1.00)	1.66 (1.00)	1.23 (1.00)
		Component (B)	0.34 (0.29)	0.28 (0.16)	0.2 8 (0.14)	0. 5 1 (0.31)	0.26 (0.21)
		Component (C)	2.43 (2.04)	2.47 (1.43)	2.55 (1.29)	2.55 (1.54)	2.25 (1.83)
		Component (D)	2.35 (1.97)	1.78 (1.03)	1.50 (0.76)	1.65 (0.99)	2.30 (1.87)
	Reaction temperature (°C)		120	115	125	120	120
	Reaction time (hour)		3	4	3	4	5

(continued)

		Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5
Second Reaction	charge (mole) : Component (D)	-	-	-	-	-
	Reaction temperature (°C)	200	200	200	200	200
	Reaction time (hour)	7	7	8	7	8

Table 2

			Ex. 6	Ex. 7	Comparative Example 1	Comparative Example 2
First Reaction	Charge (mole) ※ Numeral in parenthesis indicates molar ratio to 1 mole of component (A)	Component (A)	2.07 (1.00)	2.03 (1.00)	1.66 (1.00)	1.00 (1.00)
		Component (B)	0.29 (0.14)	0.36 (0.18)	0.51 (0.31)	0.30 (0.30)
		Component (C)	2.64 (1.28)	2.64 (1.30)	2.55 (1.54)	2.40 (2.40)
		Component (D)	1.49 (0.72)	1.43 (0.70)	1.62 (0.99)	-
	Reaction temperature (°C)		120	125	-	200
	Reaction time (hour)		4	5	-	3
Second Reaction	charge (mole) : Component (D)		-	-	-	2. 5 0 (2. 50)
	Reaction temperature (°C)		200	200	200	200
	Reaction time (hour)		8	9	7	7

Table 3

		Ex. 1	Ex. 2	Ex. 3	Ex.4	Ex. 5
Units (Molar ratio with respect to 1 mole of Component (A)	Component (A)	1.00	1.00	1.00	1.00	1.00
	Component (B)	0.28	0.16	0.15	0.30	0.21
	Component (C)	2.04	1.42	1.30	1.54	1.83
	Component (D)	1.90	0.77	0.53	0.74	1.51
Value calculated from formula (1) $B_{OH}/(A_{OH}+B_{OH})$		0.12	0.10	0.10	0.13	0.12
Molar ratio of unit derived from Component (B) in ester		0.22	0.14	0.13	0.23	0.17
Value calculated from formula (2)		0.55	0.71	0.77	0.57	0.71
Hydroxyl value (mgKOH/g)		23	32	35	37	26
Kinematic viscosity at 4 0°C (mm^2/s)		65	147	223	154	75
Acid value (mgKOH/g)		0.01	0.01	0.01	0.01	0.01
Heating test (mgKOH/g)		0.1	0.2	0.2	0.3	0.2
S R V test (μm)		410	420	410	405	415

Table 4

		Ex. 6	Ex. 7	Comparative Example 1	Comparative Example 2
Units (Molar ratio with respect to 1 mole of Component (A)	Component (A)	1.00	1.00	1.00	1.00
	Component (B)	0.14	0.18	0.30	0.30
	Component (C)	1.28	1.30	1.54	2.40
	Component (D)	0.49	0.45	0.76	2.30
Value calculated from formula (1) $B_{OH}/(A_{OH}+B_{OH})$		0.09	0.10	0.23	0.29
Molar ratio of unit derived from Component (B) in ester		0.12	0.15	0.23	0.23
Value calculated from formula (2)		0.75	0.67	1.00	1.26
Hydroxyl value (mgKOH/g)		34	31	39	13
Kinematic viscosity at 40°C (mm^2/s)		304	385	156	69
Acid value (mgKOH/g)		0.01	0.01	0.01	0.01
Heating test (mgKOH/g)		0.3	0.1	1.7	2.0
S R V test (μm)		420	410	415	550

[0068] As shown in tables 1 to 4, the esters of the Inventive Examples 1 to 7 are excellent in the lubricating and heat resistant properties, so that it is possible to prevent the degradation and to use for a long time under severe lubrication condition in a compressor. Further, as the increase of the acid value in the heat resistance test is prevented, it is possible to prevent the generation of decomposition products causing the corrosion of a metal or the like in the compressor.

[0069] On the other hand, according to the comparative examples 1 and 2, different from the esters of the Inventive Examples, the increase of the acid value is large. It is thus confirmed that the decomposition of the ester is progressed in the heat resistance test compared with the Inventive Examples.

Claims

1. An ester for a refrigerator oil, said ester being obtained from the following component (A), component (B), component (C) and component (D):

wherein said ester comprises a unit derived from said component (B) in a ratio of 0.1 to 0.4 mole, a unit derived from said component (C) in a ratio of 0.8 to 2.8 mole and a unit derived from said component (D) in a ratio of 0.3 to 2,3 mole with respect to 1.0 mole of a unit derived from said component (A):

wherein said ester has a hydroxyl value of 5 to 40 mgKOH/g; and
wherein said ester satisfies the following formulas (1) and (2).

(A) neopentyl glycol
(B) a linear dihydric alcohol having 2 to 6 carbon atoms including carbons at both terminals and hydroxyl groups connected to said carbons at said both terminals, respectively
(C) a linear dicarboxylic acid having 4 to 10 carbon atoms including carbons at both terminals and carboxyl groups connected to said carbons at said both terminals, respectively
(D) a monohydric alcohol having 6 to 12 carbon atoms

$$0.08 \leqq B_{OH}/(A_{OH}+B_{OH}) \leqq 0.15 \quad \cdots (1)$$

$$〔B_{OH}/(A_{OH}+B_{OH})〕 / 〔B_{mol}/(A_{mol}+B_{mol})〕 \leqq 0.9 \cdots(2)$$

(In said formulas (1) and (2),

A_{OH} represents a molar number of terminal hydroxyl groups derived from said component (A) in said ester;
B_{OH} represents a molar number of terminal hydroxyl groups derived from said component (B) in said ester;
A_{mol} represents a molar number of said unit derived from said component (A) in said ester; and
B_{mol} represents a molar number of said unit derived from said component (B) in said ester.)

2. A working fluid composition for a refrigerator oil, said fluid composition comprising a non-chlorine-based Freon refrigerant or a natural refrigerant, and said ester for said refrigerator oil of claim 1.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2016/066756

A. CLASSIFICATION OF SUBJECT MATTER
C10M105/42(2006.01)i, *C10N20/00*(2006.01)n, *C10N30/06*(2006.01)n, *C10N30/08*(2006.01)n, *C10N40/30*(2006.01)n

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10M105/42, C10N20/00, C10N30/06, C10N30/08, C10N40/30

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2016
Kokai Jitsuyo Shinan Koho	1971-2016	Toroku Jitsuyo Shinan Koho	1994-2016

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2014/017596 A1 (JX Nippon Oil & Energy Corp.), 30 January 2014 (30.01.2014), & US 2015/0184103 A1 & EP 2878652 A1 & CN 104508094 A & KR 10-2015-0036234 A	1-2
A	WO 2014/156738 A1 (JX Nippon Oil & Energy Corp.), 02 October 2014 (02.10.2014), & EP 2980192 A1 & CN 104995288 A & KR 10-2015-0133190 A	1-2
A	JP 2001-501991 A (Exxon Chemical Patents Inc.), 13 February 2001 (13.02.2001), & US 5698502 A & EP 938536 A1 & KR 10-2000-0036032 A & CN 1233273 A	1-2

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:

"A"	document defining the general state of the art which is not considered to be of particular relevance
"E"	earlier application or patent but published on or after the international filing date
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O"	document referring to an oral disclosure, use, exhibition or other means
"P"	document published prior to the international filing date but later than the priority date claimed
"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&"	document member of the same patent family

Date of the actual completion of the international search 20 June 2016 (20.06.16)	Date of mailing of the international search report 28 June 2016 (28.06.16)
Name and mailing address of the ISA/ Japan Patent Office 3-4-3,Kasumigaseki,Chiyoda-ku, Tokyo 100-8915,Japan	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (January 2015)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2016/066756

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2013-181133 A (JX Nippon Oil & Energy Corp.), 12 September 2013 (12.09.2013), & US 2015/0014575 A1 & EP 2821464 A1 & CN 104145006 A & KR 10-2014-0133828 A	1-2

Form PCT/ISA/210 (continuation of second sheet) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 10008084 A **[0007]**
- WO 2014017596 B1 **[0007]**