SPECIFICATION

Refrigeration lubricant composition

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a refrigeration lubricant composition. More specifically, the present invention relates to a refrigeration lubricant composition for use with a chlorine-free hydrofluorocarbon refrigerant, a refrigerant working fluid containing the refrigeration lubricant composition, and a refrigerating apparatus including the refrigerant working fluid.

2. Description of the Related Art

Refrigerants containing chlorofluorocarbon have been used for refrigerators, air conditioning equipment, and the like. However, in recent years, the replacement of chlorofluorocarbon refrigerants with chlorine-free hydrofluorocarbon refrigerants such as those containing 1,1,1,2-tetrafluoroethane (R-134a), pentafluoroethane (R-125), difluoromethane (R-32), and mixtures thereof has been promoted because of problems such as the depletion of the ozone layer. Consequently, a variety of refrigeration lubricant compositions (hereinafter may be referred to as "refrigeration oils") containing a polyol ester, which has good compatibility with chlorine-free hydrofluorocarbon refrigerants, as a base stock have been proposed.

In addition to the above-mentioned compatibility with chlorine-free hydrofluorocarbon refrigerants, a variety of properties

such as lubricity, thermal stability, hydrolytic stability, low-temperature fluidity, and electric insulation properties are required for the refrigeration oils in order to ensure the stability of the above-mentioned refrigerators, air conditioning equipment, and the like. Among these, in view of hydrolytic stability and compatibility with chlorine-free hydrofluorocarbon refrigerants, hindered esters obtained from a carboxylic acid having a side chain and pentaerythritol and having excellent thermal resistance have been put to practical use. For example, Japanese Laid-Open Patent Publication No. 10-8084 discloses refrigeration oils containing an ester obtained from pentaerythritol and a mixed fatty acid of 2-ethylhexanoic acid and 3,5,5-trimethylhexanoic acid as the main component, and discloses that such refrigeration oils have good stability at high temperatures. Japanese Laid-Open Patent Publication No. 6-330061 discloses refrigeration oils containing an ester obtained from pentaerythritol and a mixed fatty acid of a linear or branched fatty acid having 6 to 8 carbon atoms and 3,5,5-trimethylhexanoic acid as the main component. The publication discloses that such refligeration oils have excellent compatibility with refrigerants and good electric insulating properties.

In line with increasing awareness of environmental issues of recent years, refrigerators, air conditioning equipment, and the like are required to have energy-saving properties. In the refrigeration oils, decreasing the viscosity thereof is the most efficient way to make a contribution to the energy-saving properties of refrigerators and the like. Therefore, there is an attempt to decrease the viscosity of the refrigeration oils.

In order to decrease the viscosity of the refrigeration oils, it is effective to use esters obtained from a dihydric alcohol such as neopentyl glycol that have lower viscosity than penthaerythritol esters

and have excellent hydrolytic stability, thermal stability, and other properties. However, these esters have poor electric insulation properties because of their low volume resistivity. Thus, a reduction of the viscosity for making a contribution to energy saving decreases the electric insulation properties, which is an effect contrary to the intended purpose. Therefore, it is very difficult to obtain a refrigeration oil having low viscosity and excellent electric insulation properties.

Moreover, since the refrigeration oils are used for apparatuses for cooling, it is critical for the refrigeration oils to have stability at low temperatures, and in particular, the refrigeration oils are required to have a property of not causing precipitation of crystals even when exposed to such a low temperature region for a long period of time. However, the mixed esters obtained from the combination of a polyhydric alcohol with specific carboxylic acids as described in Japanese Laid-Open Patent Publication No. 10-8084 and Japanese Laid-Open Patent Publication No. 6-330061 mentioned above have not been sufficiently examined for their ability of maintaining low-temperature stability over a long period of time.

Thus, although there has been a demand for a refrigeration oil having excellent low-temperature stability and low viscosity, and furthermore, high electric insulation properties (high volume resistivity), it is difficult to obtain the same, as described above.

SUMMARY OF THE INVENTION

It is an aim of the embodiments disclosed herein to provide a refrigeration lubricant composition having low viscosity and high volume resistivity and also having excellent long-term stability in a low temperature region, and more particularly a refrigeration lubricant

composition for refrigerators employing a chlorine-free hydrofluorocarbon refrigerant. It is another aim of the embodiments disclosed herein to provide a refrigerant working fluid containing the refrigeration lubricant composition, and a refrigerant compression type refrigerating apparatus including the refrigerant working fluid.

The inventors carefully examined the volume resistivity and the low-temperature stability of ester lubricant compositions having low viscosity for use in refrigerators employing a chlorine-free hydrofluorocarbon refrigerant, and conducted molecular design of esters in which various combinations of alcohols and carboxylic acids are examined. As a result, the inventors found that a mixed ester having low viscosity and having high volume resistivity and excellent long-term low-temperature stability can be obtained from the combination of a mixed alcohol comprising neopentyl glycol, pentaerythritol, and dipentaerythritol that satisfy a certain quantitative relationship with a saturated monocarboxylic acid having 5 to 10 carbon atoms, and thus the disclosure was accomplished.

In one aspect, there is provided a refrigeration lubricant composition comprising a mixed ester obtained from a mixed alcohol and a saturated monocarboxylic acid having 5 to 10 carbon atoms as a main component, wherein the mixed alcohol comprises 1 to 90 mol% of neopentyl glycol, 10 to 80 mol% of pentaerythritol, and 0.01 to 20 mol% of dipentaerythritol and satisfies the following relation:

$$0.2 \leqq \frac{(\text{Mol\% of pentaerythritol})}{\{(\text{Mol\% of neopentyl glycol}) \times (\text{Mol\% of dipentaerythritol})\}} \leqq 7.0 \qquad (1)$$

and the composition has a kinematic viscosity at 40°C of 6 to 28 mm^2/s.

In a preferred embodiment, the saturated monocarboxylic acid

comprises at least 85 mol% of a saturated monocarboxylic acid having a side chain at the α-position.

In a preferred embodiment, the mixed ester comprises 10 to 65 mol% of the ester having a molecular weight of 370 to 1000.

Disclosed herein is a refrigerant working fluid comprising the refrigeration lubricant composition and a chlorine-free hydrofluorocarbon refrigerant.

Disclosed herein is a refrigerant compression type refrigerating apparatus comprising a compressor, a condenser, an expansion mechanism, an evaporator, and wherein the refrigerant working fluid.

The disclosed refrigeration lubricant composition has low viscosity, high volume resistivity, and excellent long-term low-temperature stability. Furthermore, it also has excellent compatibility with chlorine-free hydrofluorocarbon refrigerants, thermal resistance, and lubricity, which are required for a refrigeration lubricant composition. Therefore, the disclosed composition is useful for a lubricant for refrigerators employing a chlorine-free hydrofluorocarbon refrigerant, wherein the chlorine-free hydrofluorocarbon refrigerant contains at least one of 1,1,1,2-tetrafluoroethane and difluoromethane, or useful for a refrigerant working fluid obtained by mixing this lubricant with a chlorine-free hydrofluorocarbon refrigerant. Furthermore, the disclosed composition also contributes to energy-saving properties of a variety of types of refrigerating apparatuses.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Hereinafter, a mixed ester contained in the composition of the present invention, a refrigeration lubricant composition containing the

mixed ester, a refrigerant working fluid containing the composition, and a refrigerant compression type refrigerating apparatus including the refrigerant working fluid will be described.

(Mixed Ester)

The mixed ester contained in the refrigeration lubricant composition of the present invention is obtained from a mixed alcohol and a saturated monocarboxylic acid having 5 to 10 carbon atoms, wherein the mixed alcohol comprises 1 to 90 mol% of neopentyl glycol, 10 to 80 mol% of pentaerythritol, and 0.01 to 20 mol% of dipentaerythritol and satisfies the following relation:

$$0.2 \leqq \frac{(\text{Mol\% of pentaerythritol})}{[(\text{Mol\% of neopentyl glycol}) \times (\text{Mol\% of dipentaerythritol})]} \leqq 7.0 \quad (1)$$

In order to solve the problem that a dihydric alcohol such as neopentyl glycol reduces the volume resistivity of the resultant ester, the inventors of the present invention conducted molecular design of esters and found that when the above-noted relation was satisfied, an ester having low viscosity and having excellent long-term low-temperature stability could be obtained without any reduction of volume resistivity. In more detail, the inventors found that a mixed ester having low viscosity, high (i.e., unreduced) volume resistivity, and excellent long-term low-temperature stability can be obtained from a specific mixed alcohol and a saturated monocarboxylic acid having 5 to 10 carbon atoms, wherein the specific mixed alcohol is a combination of neopentyl glycol, pentaerythritol and dipentaerythritol, and the amounts of which satisfy the above relation.

In the mixed ester contained in the refrigeration lubricant composition of the present invention, the saturated monocarboxylic

acid that is a raw material of the mixed ester preferably contains at least 85 mol% of a saturated monocarboxylic acid having a side chain at the α-position in view of hydrolytic stability.

The mixed ester contained in the refrigeration lubricant composition of the present invention preferably contains 10 to 65 wt% of the mixed ester having a molecular weight of 370 to 1000 in view of long-term low-temperature stability, volume resistivity, and thermal resistance.

Hereinafter, a method for producing the mixed ester will be described.

A mixed alcohol that is a raw material of the mixed ester comprises 1 to 90 mol% of neopentyl glycol, 10 to 80 mol% of pentaerythritol, and 0.01 to 20 mol% of dipentaerythritol, as described above. When a mixed ester is prepared by using the above-mentioned alcohols but the amounts of the alcohols are outside of the above-mentioned range, the resultant ester has poor lubricity or low level of thermal resistance. Alternatively, the ester provides poor energy-saving properties when the ester is put to practical use. Furthermore, the ester does not provide satisfactory volume resistivity and long-term low-temperature stability.

The saturated monocarboxylic acid having 5 to 10 carbon atoms that is a raw material of the mixed ester is not particularly limited. Either or both of a linear saturated monocarboxylic acid and a saturated monocarboxylic acid having a side chain can be used. In view of long-term low-temperature stability, compatibility with chlorine-free hydrofluorocarbon refrigerants, and corrosion resistance, a linear saturated monocarboxylic acid having 5 to 7 carbon atoms or a branched saturated monocarboxylic acid having 7 to 10 carbon atoms is preferable. A saturated monocarboxylic acid having at least 5 carbon

atoms can provide a mixed ester having good lubricity. A saturated monocarboxylic acid having not more than 10 carbon atoms can provide a mixed ester having excellent low-temperature stability and compatibility with chlorine-free hydrofluorocarbon refrigerants.

Examples of the saturated monocarboxylic acid having 5 to 10 carbon atoms include pentanoic acid, 2-methylbutanoic acid, 3-methylbutanoic acid, hexanoic acid, 2-methylpentanoic acid, 3-methylpentanoic acid, 4-methylpentanoic acid, 2-ethylbutanoic acid, 3-ethylbutanoic acid, heptanoic acid, 2-methylhexanoic acid, 3-methylhexanoic acid, 4-methylhexanoic acid, 5-methylhexanoic acid, 2,2-dimethylpentanoic acid, 2-ethylpentanoic acid, 3-ethylpentanoic acid, 2-ethylhexanoic acid, 2-methylheptanoic acid, 3-methylheptanoic acid, 4-methylheptanoic acid, 5-methylheptanoic acid, 6-methylheptanoic acid, 2,2-dimethylhexanoic acid, 3,5-dimethylhexanoic acid, nonanoic acid, isononanoic acid, decanoic acid, and neodecanoic acid. Preferably, a saturated monocarboxylic acid having a side chain at the α-position, and more preferably 2-ethylhexanoic acid, is used because of good lubricity and hydrolytic stability of the resultant mixed ester and in view of the anti-corrosiveness to metal. The above-mentioned saturated monocarboxylic acids having 5 to 10 carbon atoms may be used alone, or may be used in combination of two or more thereof giving consideration to hydrolysis resistance, lubricity, compatibility with chlorine-free hydrofluorocarbon refrigerants, thermal resistance, low-temperature stability, viscosity, and the like.

By combining the above-described mixed alcohol and the above-described saturated monocarboxylic acid having 5 to 10 carbon atoms, a mixed ester having a high level of volume resistivity can be obtained although neopentyl glycol is employed as a raw material, and the resultant mixed ester has excellent long-term low-temperature

stability. For example, according to the intended viscosity, a mixed alcohol obtained by mixing neopentyl glycol, pentaerythritol, and dipentaerythritol such that the relation (1) above is satisfied is reacted with a saturated monocarboxylic acid having 5 to 10 carbon atoms. Preferably, the saturated monocarboxylic acid contains at least 85 wt% of a saturated monocarboxylic acid having a side chain at the α-position. Alternatively, the saturated monocarboxylic acid can be a single or plural saturated monocarboxylic acid(s) that can provide a mixed ester that contains 10 to 65 wt% of ester(s) having a molecular weight of 370 to 1000.

The reaction is performed by ordinary esterification reaction or transesterification. The ratio between the above-described mixed alcohol and the above-described saturated monocarboxylic acid having 5 to 10 carbon atoms may be determined as appropriate such that the resultant mixed ester has a hydroxyl value of 5.0 mgKOH/g or less and an acid value of 0.05 mgKOH/g or less.

Specifically, the mixed ester used in the present invention is obtained in the following manner. First, the carboxylic acid is mixed with the mixed alcohol such that the carboxyl group in the carboxylic acid is 1.0 to 1.5 equivalents, preferably 1.05 to 1.3 equivalents in view of production efficiency and economic efficiency, with respect to one equivalent of hydroxyl group in the mixed alcohol, and then a catalyst is added thereto, if necessary. This mixture is allowed to react for 3 to 15 hours at 220 to 260°C under a nitrogen gas stream, and at the point when the hydroxyl value of the reaction mixture becomes 2.0 mgKOH/g or less, excess carboxylic acid is removed under a reduced pressure. Then, after neutralization with an alkali, operations such as adsorption treatment using activated clay, acid clay, and a synthesized adsorbent and steaming are performed either alone or in combination.

(Refrigeration Lubricant Composition)

The refrigeration lubricant composition of the present invention contains the above-described mixed ester as the main component and may contain, for example, an additive and an ester other than the mixed ester, if necessary. The specific amount of the "main component" is 50 wt% or more, preferably 70 wt% or more, and more preferably 90 wt% or more based on the entire refrigeration lubricant composition. The amount may be 100 wt%.

Examples of the ester other than the above-described mixed ester that may be contained in the refrigeration lubricant composition of the present invention include esters obtained from neopentyl polyol having 2 to 8 hydroxyl groups and having 5 to 15 carbon atoms that excludes neopentyl glycol, pentaerythritol, and dipentaerythritol and a monocarboxylic acid or a polyvalent carboxylic acid. Examples of such neopentyl polyol include 2,2-diethyl-1,3-propanediol, 2-n-butyl-2-ethyl-1,3-propanediol, trimethylolethane, triethylolethane, trimethylolpropane, tripentaerythritol, and bispentaerythritol. The ester may be contained as appropriate within the range of not inhibiting the properties of the refrigeration lubricant composition of the present invention.

Examples of the additive that may be contained in the refrigeration lubricant composition of the present invention include a phenolic antioxidant, a metal deactivator such as benzotriazole, thiadiazole, and dithiocarbamate, an acid scavenger such as epoxy compounds and carbodiimides, and a phosphorous extreme pressure agent. The additive is contained in any ratio.

The kinematic viscosity at 40°C of the refrigeration lubricant composition of the present invention is 6 to 28 mm^2/s. In view of

excellent lubricity and compatibility of the composition with chlorine-free hydrofluorocarbon refrigerants, and in view of good startability and energy-saving properties when the lubrication oil composition is used for refrigerators, the kinematic viscosity at 40°C is preferably 6.5 to 27.5 mm^2/s, and more preferably 7 to 27 mm^2/s.

There is no particular limitation regarding the acid value of the refrigeration lubricant composition of the present invention. The acid value is preferably 0.05 mgKOH/g or less, more preferably 0.03 mgKOH/g or less, and even more preferably 0.01 mgKOH/g or less. A refrigeration lubricant composition having an acid value of 0.05 mgKOH/g or less is less likely to corrode metals and has good hydrolytic stability.

There is no particular limitation regarding the hydroxyl value of the refrigeration lubricant composition of the present invention. The hydroxyl value is preferably 5.0 mgKOH/g or less, more preferably 3.0 mgKOH/g or less, even more preferably 2.0 mgKOH/g or less, and most preferably 1.0 mgKOH/g or less. When the hydroxyl value is 5.0 mgKOH/g or less, the composition has sufficient electric insulation property without deteriorating the volume resistivity of the composition. Therefore, in the equipment in which the composition is employed, there is no possibility of an adverse effect such as dissolving a sealing material that is made of an organic material. Also, there is no possibility of an adverse effect on additives that may be contained in the composition.

(Refrigerant Working Fluid)

The refrigerant working fluid of the present invention comprises the above-described refrigeration lubricant composition and a chlorine-free hydrofluorocarbon refrigerant. There is no particular

limitation regarding the mixing ratio between the refrigeration lubricant composition and the chlorine-free hydrofluorocarbon refrigerant, but the weight ratio of the refrigeration lubricant composition and the chlorine-free hydrofluorocarbon refrigerant is preferably from 10:90 to 90:10. When the amount of the chlorine-free hydrofluorocarbon refrigerant is higher than the above-mentioned range, the viscosity of the resultant refrigerant working fluid is reduced, which may lead to poor lubrication. When the amount is lower than the above described range, refrigerating efficiency may deteriorate when the resultant refrigerant working fluid is used for refrigerating apparatuses.

Specific examples of the chlorine-free hydrofluorocarbon refrigerant include 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), and 1,1-difluoroethane (R-152a). These refrigerants may be used either alone or as mixed refrigerants of two or more thereof.

The above-mentioned mixed refrigerants are commercially available, and, for example, R-407C (R-134a/R-125/R-32 = 52 wt%/25 wt%/23 wt%), R-410A (R-125/R-32 = 50 wt%/50 wt%), R-404A (R-125/R-143a/R-134a = 44 wt%/52 wt%/4 wt%), R-407E (R-134a/R-125/R-32 = 60 wt%/15 wt%/25 wt%), and R-410B (R-32/R-125 = 45 wt%/55 wt%) are used. Among these, mixed refrigerants containing at least one of R-134a and R-32 are particularly preferable.

(Refrigerant Compression Type Refrigerating Apparatus)

The refrigerant compression type refrigerating apparatus of the present invention is provided with a compressor, a condenser, an expansion mechanism, and an evaporator and is configured such that

the above-described refrigerant working fluid, which is the refrigerant in the refrigerating apparatus, circulates through these components. This refrigerating apparatus may further include a drier. Examples of such a refrigerating apparatus include air conditioning equipment such as room air conditioners and packaged air conditioners; low temperature apparatuses such as refrigerators and freezers; industrial refrigerators; and air conditioners for automobiles such as hybrid cars and electric cars.

Examples

Hereinafter, the present invention will be described more specifically by way of examples.

The test methods for evaluating esters produced in the examples and the comparative examples will be described below:

<Kinematic viscosity and viscosity index> The kinematic viscosity at 40°C and that at 100°C are measured with a Cannon-Fenske viscometer according to JIS K-2283, and the viscosity index is calculated from the resultant values.

<Acid value> The acid value is measured according to JIS C-2101.

<Hydroxyl value> The hydroxyl value is measured according to JIS K-0070.

<Color number (APHA)> The color number (APHA) is measured according to JOCS 2.2.1.4-1996.

<Volume resistivity> The volume resistivity (TΩ•m) at 25°C is measured according to JIS C-2101.

<Pour point> The pour point is measured according to JIS K-2269.

<Long-term low-temperature test> First, 400 g of a sample ester, the moisuture content of which was adjusted to 100 ppm or less, is placed in a square can made of steel and allowed to stand for 1000 hours in a

low temperature storage at −28°C, and then checked visually to determine whether or not crystals are precipitated.

<Two-phase separation temperature> First, 0.6 g of a sample ester and 2.4 g of refrigerant R-134a were enclosed in a thick PYREX (registered trademark) tube (entire length: 300 mm, outer diameter of 10 mm, inner diameter of 6 mm) cooled in an ethanol bath containing dry ice and warmed or cooled at a rate of 1°C/min. Then, the two-phase separation temperatures at a high temperature and a low temperature were measured visually within a temperature range from −70°C to +80°C.

<Sealed tube test> First, 10 g of a sample ester, the moisuture content of which has been adjusted to 200 ppm or less, 5 g of fluorocarbon R-410A, and one each of iron, copper, and aluminum metal pieces having a length of 10 mm are put in a glass tube and the grass tube is sealed. This is heated at 175°C for 14 days, and then the acid value and the color number (APHA) of the fluorocarbon-containing sample from which the metal pieces were removed are measured.

<Falex friction test> The Falex friction test was performed according to ASTM D-2670 while blowing R-134a into a sample ester at a rate of 150 mL/min. The temperature of the sample is set at 100°C, and an operation under a load of 250 pound is carried out for 2 hours after a trial operation under a load of 150 pound for one minute, and the wear amount of the pin after the end of the operation is measured.

Synthesis Example 1: Preparation of Ester

First, alcohols and saturated monocarboxylic acids shown in Table 1 were placed in a one-liter four-necked flask provided with a thermometer, a nitrogen inlet tube, a stirrer and a condenser such that the ratio of the hydroxyl groups in the mixed alcohol and the carboxyl

groups in the saturated monocarboxylic acid is 1:1.1 in the equivalent ratio, and then reacted under a nitrogen gas stream at 220°C at an atmospheric pressure while water generated by the reaction was removed by distillation. During the reaction, the hydroxyl value of the reaction mixture was monitored, and the reaction was stopped at the point when the hydroxyl value became lower than 2.0 mgKOH/g. Then, stripping was performed under a reduced pressure of 1 to 5 kPa to remove unreacted carboxylic acid for one hour. The resultant reaction mixture was washed with an aqueous solution of potassium hydroxide. Washing was repeated five times so that the pH of the discharged water became neutral. Then, the resultant ester layer was dried at 100°C under a reduced pressure of 1 kPa. Then, acid clay and a silica-alumina adsorbent were added thereto for an adsorption treatment such that each of them is contained in an amount of 1.0 wt% with respect to the theoretical amount of an ester to be obtained. The adsorption treatment temperature, pressure, and adsorption treatment time were 100°C, 1 kPa, and 3 hours, respectively. Thereafter, the mixture was filtrated using a one-micron filter, and thus an ester (ester A) was obtained. The kinematic viscosity at 40°C and that at 100°C of the obtained ester A were measured according to the above-described method. Table 1 shows the results.

Synthesis Examples 2 to 7

Esters (esters B to G) were obtained in the same manner as in Synthesis Example 1 except that alcohols and a single or plural saturated monocarboxylic acid(s) shown in Table 1 were used. The kinematic viscosity at 40°C and that at 100°C of each ester were measured according to the above-described method. Table 1 also shows the results.

Comparative Synthesis Examples 1 to 5

Esters (esters H to L) were obtained in the same manner as in Synthesis Example 1 except that a single or plural alcohol(s) and a single or plural saturated monocarboxylic acid(s) shown in Table 1 were used. The kinematic viscosity at 40°C and that at 100°C of each ester were measured according to the above-described method. Table 1 also shows the results.

Table 1

		Mixed ester								
		Mixed alcohol				Saturated monocarboxylic acid (mol%)	Ester	Content of ester having molecular weight of 370 to 1000 (mol%)	Measurement results	
		Components*1 (mol%)			Value of relation*2				Kinematic viscosity (mm^2/s)	
		NPG	PE	diPE					40°C	100°C
Synthesis Ex.	1	87.0	12.9	0.1	1.48	2-Ethylhexanoic acid (95) 3,5,5-Trimethylhexanoic acid (5)	A	12.9	10.62	2.571
	2	68.0	30.5	1.5	0.30	2-Ethylhexanoic acid (97) Caproic acid (3)	B	30.8	15.23	3.235
	3	50.0	48.0	2.0	0.48	2-Ethylhexanoic acid (100)	C	48.0	22.01	4.055
	4	47.0	50.0	3.0	0.35	2-Ethylhexanoic acid (100)	D	50.0	23.14	4.187
	5	89.85	10.1	0.05	2.25	2-Ethylhexanoic acid (88) 3,5,5-Trimethylhexanoic acid (12)	E	10.1	10.68	2.593
	6	70.0	29.1	0.9	0.46	2-Ethylhexanoic acid (90) 2-Methylhexanoic acid (7) Pentanoic acid (3)	F	29.5	14.22	3.111
	7	80.0	19.0	1.0	0.24	2-Ethylhexanoic acid (93) 3,5,5-Trimethylhexanoic acid (5) 2,5,5-Trimethylhexanoic acid (1) 6,6-Dimethylheptanoic acid (1)	G	19.0	12.86	2.921
Com. Synthesis Ex.	1	100	—	—	—	2-Ethylhexanoic acid (100)	H	0.0	7.473	2.043
	2	47.0	53.0	—	—	2-Ethylhexanoic acid (100)	I	53.0	24.85	4.349
	3	92.0	—	8.0	0	2-Ethylhexanoic acid (90) Pentanoic acid (10)	J	3.7	10.21	2.544
	4	49.2	50.7	0.1	10.30	2-Ethylhexanoic acid (100)	K	50.7	21.50	4.019
	5	32.0	65.1	2.9	0.70	2-Ethylhexanoic acid (100)	L	65.1	30.20	4.903

*1···NPG: Neopentyl glycol, PE: Pentaerythritol, diPE: Dipentaerythritol

*2···Mol% of PE/(Mol% of NPG × Mol% of diPE)

As seen from Table 1, the esters (esters A to G) of Synthesis Examples 1 to 7 satisfy the requirements for the ester employed in the present invention, but the esters (esters H to L) of Comparative Synthesis Examples 1 to 5 do not satisfy the requirements. In other words, the esters H to J of Comparative Synthesis Examples 1 to 3 do not employ the specific three alcohols. As for the ester K of Comparative Synthesis Example 4, the value of the relation is 10.30, which does not fall within the range of 0.2 to 7.0. The ester L of Comparative Synthesis Example 5 has a high viscosity of 30.20 mm^2/s at 40°C and thus cannot satisfy the viscosity range (6 to 28 mm^2/s) required in the lubricant composition of the present invention.

Example 1: Evaluation of Lubricant

The ester A obtained in Synthesis Example 1 was designated as lubricant 1. Regarding the lubricant 1, kinematic viscosity at 40°C and that at 100°C, viscosity index, color number (APHA), acid value, hydroxyl value, volume resistivity, pour point, and two-phase separation temperature were measured according to the above-described methods, and furthermore, the long-term stability test, sealed tube test, and Falex test were performed. Table 2 shows the results.

Examples 2 to 7: Evaluation of Lubricants

The esters (esters B to G) obtained in Synthesis Examples 2 to 7 were designated as lubricants 2 to 7. Regarding each lubricant, kinematic viscosity at 40°C and that at 100°C, viscosity index, color number (APHA), acid value, hydroxyl value, volume resistivity, pour point, and two-phase separation temperature were measured according to the above-described methods, and furthermore, the long-term stability test, sealed tube test, and Falex test were performed. Table

2 also shows the results.

Comparative Examples 1 to 5

The esters (esters H to L) obtained in Comparative Synthesis Examples 1 to 5 were designated as lubricants 8 to 12. Regarding each lubricant, kinematic viscosity at 40°C and that at 100°C, viscosity index, color number (APHA), acid value, hydroxyl value, volume resistivity, pour point, and two-phase separation temperature were measured according to the above-described methods, and furthermore, the long-term stability test, sealed tube test, and Falex test were performed. Table 2 also shows the results.

Table 2

		Ester content (wt%)	Lubricant	Measurement results													
				Kinematic viscosity (mm^2/s)		Viscosity index	Color number (APHA)	Acid value (mgKOH/g)	Hydroxyl value (mgKOH/g)	Volume resistivity (TΩ·m)	Pour point (℃)	Long-term low-temp. test *1	Two-phase separation temperature		Sealed tube test		Falex test
				40℃	100℃								Low temp. (℃)	High temp (℃)	Color number (APHA)	Acid value (mgKOH/g)	Pin wear amount (mg)
Ex.	1	A (100)	1	10.62	2.571	54	43	0.01	0.2	1.9	<−50	A	<−50	80<	64	0.11	18
	2	B (100)	2	15.23	3.235	61	63	0.01	0.5	3.4	<−50	A	−38	80<	75	0.13	17
	3	C (100)	3	22.01	4.055	66	40	0.01	0.8	4.9	<−50	A	−28	80<	68	0.12	16
	4	D (100)	4	23.14	4.187	69	39	0.01	0.7	5.3	<−50	A	−27	80<	63	0.13	15
	5	E (100)	5	10.68	2.593	58	42	0.01	0.1	1.4	<−50	A	<−50	80<	68	0.12	19
	6	F (100)	6	14.22	3.111	63	54	0.01	0.4	2.7	<−50	A	−48	80<	76	0.09	17
	7	G (100)	7	12.86	2.921	62	49	0.01	0.2	2.5	<−50	A	<−50	80<	75	0.08	18
Com. Ex.	1	H (100)	8	7.473	2.043	48	49	0.01	0.6	0.3	<−50	A	<−50	80<	79	0.15	20
	2	I (100)	9	24.85	4.349	67	46	0.01	0.5	4.2	−47.5	C	−29	80<	70	0.14	15
	3	J (100)	10	10.21	2.544	64	68	0.01	0.4	0.4	<−50	A	<−50	80<	90	0.17	19
	4	K (100)	11	21.50	4.019	69	40	0.01	0.8	5.4	<−50	C	−29	80<	69	0.13	17
	5	L (100)	12	30.20	4.903	76	40	0.01	0.9	6.3	−40	B	−23	80<	65	0.11	14

*1···Holding at −28 ℃ for 1000 hours. The indication "A" denotes that no precipitation occurs, the indication "B" denotes that precipitation occurs, and the indication "C" denotes that gelation or solidification occurs.

As is apparent from the results in Table 2, it is found that the lubricants (lubricants 1 to 7) of Examples 1 to 7 that satisfy the requirements of the present invention have low viscosity and high volume resistivity and also have excellent stability with no precipitation occurring even in the long-term low-temperature test. Furthermore, these lubricants 1 to 7 have a low pour point; excellent compatibility with hydrofluorocarbon refrigerants, which is indicated by the two-phase separation temperature; and less susceptibility to deterioration due to thermal oxidation, which is indicated by the results of the sealed tube test; and the lubricants satisfy the other performances required for a refrigeration lubricant. Therefore, they are regarded as excellent lubricants. In contrast, as for the lubricants 8 to 10 comprising the esters (esters H to J) that were prepared without using the three specific alcohols employed in the present invention, the volume resistivity was low or precipitation occurred in the long-term low-temperature test. As for the lubricant 11 (i.e., the ester K) derived from the three specific alcohols but does not satisfy the relation, precipitation occurred in the long-term low-temperature test. The lubricant 12 was derived from the above-described three specific alcohols and satisfy the relation, but the kinematic viscosity at 40°C was high, and thus, the low-temperature stability was poor.

The refrigeration lubricant composition of the present invention has low viscosity, high volume resistivity, and excellent low-temperature stability. Furthermore, it has good compatibility with hydrofluorocarbons, particularly with chlorine-free hydrofluorocarbons, so that it is preferably used for a lubricant for refrigerators employing a chlorine-free hydrofluorocarbon refrigerant or used for a refrigerant working fluid obtained by mixing this lubricant with a chlorine-free hydrofluorocarbon refrigerant. Specifically, the refrigeration

lubricant composition of the present invention and the refrigerant working fluid containing the lubricant composition and a chlorine-free hydrofluorocarbon refrigerant can be used for air conditioning equipment such as room air conditioners and packaged air conditioners; low temperature apparatuses such as refrigerators and freezers; industrial refrigerators; and compressors of air conditioners for automobiles such as hybrid cars and electric cars.

The invention may be embodied in other forms without departing from the spirit or essential characteristics thereof. The embodiments disclosed in this application are to be considered in all respects as illustrative and not limiting. The scope of the invention is indicated by the appended claims rather than by the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are intended to be embraced therein.

What is claimed is:

1. A refrigeration lubricant composition comprising a mixed ester obtained from a mixed alcohol and a saturated monocarboxylic acid having 5 to 10 carbon atoms as a main component,

wherein the mixed alcohol comprises 1 to 90 mol% of neopentyl glycol, 10 to 80 mol% of pentaerythritol, and 0.01 to 20 mol% of dipentaerythritol and satisfies the following relation:

$$0.2 \leqq \frac{(\text{Mol\% of pentaerythritol})}{[(\text{Mol\% of neopentyl glycol}) \times (\text{Mol\% of dipentaerythritol})]} \leqq 7.0 \quad (1)$$

and the composition has a kinematic viscosity at 40°C of 6 to 28 mm^2/s.

2. The refrigeration lubricant composition of claim 1, wherein the saturated monocarboxylic acid comprises at least 85 mol% of a saturated monocarboxylic acid having a side chain at the α-position.

3. The refrigeration lubricant composition of claim 1 or 2, wherein the mixed ester comprises 10 to 65 mol% of an ester having a molecular weight of 370 to 1000.

4. A refrigerant working fluid comprising the refrigeration lubricant composition of any one of claims 1 to 3 and a chlorine-free hydrofluorocarbon refrigerant.

5. A refrigerant compression type refrigerating apparatus comprising a compressor, a condenser, an expansion mechanism, an evaporator, and the refrigerant working fluid of claim 4.

ABSTRACT OF THE DISCLOSURE

Refrigeration Lubricant Composition

The present invention provides a refrigeration lubricant composition comprising a mixed ester obtained from a mixed alcohol and a saturated monocarboxylic acid having 5 to 10 carbon atoms as a main component, wherein the mixed alcohol comprises 1 to 90 mol% of neopentyl glycol, 10 to 80 mol% of pentaerythritol, and 0.01 to 20 mol% of dipentaerythritol and satisfies the following relation:

$$0.2 \leqq \frac{(\text{Mol\% of pentaerythritol})}{[(\text{Mol\% of neopentyl glycol}) \times (\text{Mol\% of dipentaerythritol})]} \leqq 7.0 \qquad (1)$$

and the composition has a kinematic viscosity at 40°C of 6 to 28 mm^2/s.