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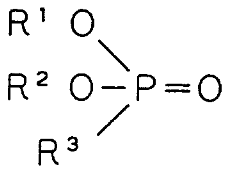
(54) Lubricating oil composition and use thereof.

(57) The present invention provides a lubricating oil composition for refrigerating machine capable of enhancing the anti-wear property of the entire system when used together with 1,1,1,2-tetrafluoroethane (HFC-134a) which does not act as an extreme-pressure agent.

This composition exhibits an anti-wear property superior to that of the existing lubricating oil composition for refrigerating machine using CFC-12.

The ester expressed in any one of Formulae (I), (V), (VI) is used as the base oil or as an additive to the base oil. (The symbols in the formulae are as specified in Specification herein.)



(I)

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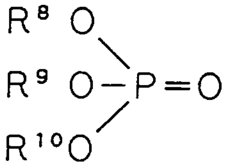
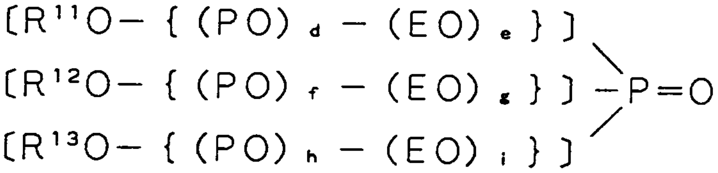
Jouve, 18, rue Saint-Denis, 75001 PARIS



$$(R^{8}O)(R^{9}O)(R^{10}O)P=O$$

(V)



$$[R^{11}O-\{(PO)_{d}-(EO)_{e}\}][R^{12}O-\{(PO)_{f}-(EO)_{g}\}][R^{13}O-\{(PO)_{h}-(EO)_{i}\}]P=O$$

(VI)

BACKGROUND OF THE INVENTION

This invention relates to a lubricating oil composition for refrigerating machine using 1,1,1.2-tetrafluoroethane (HFC-134a) as refrigerant.

Hitherto, as the refrigerant for refrigerating machine, chlorofluorocarbons containing fluorine and chlorine have been used, such.as trichloromonofluoromethane (CFC-11), dichlorodifluoromethane (CFC-12), and monochlorodifluoromethane (HCFC-22). Of them, CFC-11 and CFC-12 are designated as fully halogenated fluorocarbons because they destroy the ozone layer in the stratosphere, and their use is being limited at the present, and it is nearly decided that their use will be completely banned-in the future. Besides, HCFC-22 is also likely to be designated as the subject of restriction in the future.

Of these chlorofluorocarbons, CFC-12 is widely used in the refrigerating machines such as household refrigerators and automotive air-conditioners, and as the substitute after the use is banned, a chlorine-free 1,1,1,2-tetrafluoroethane (HFC-134a) is expected to be used.

The HFC-134a, not containing chlorine in its molecule, does not act as extreme-pressure agent, unlike CFC-12, which poses the problem of wear of metallic parts exposed inside the compressor. The HFC-134a is also inferior in solubility with existing mineral oils, synthetic oils, and other lubricating oils for refrigerating machines (base oils), and ordinary additives blended in such lubricating oils.

Of these problems, the solubility may be nearly solved by using, as the substitutes for hitherto used base oils, for examples, polyalkylene glycol (see Japanese Patent Unexamined Publications No. 102296/1990, 276880/1990), ester base fluid (see Japanese Patent Unexamined Publications No. 24197/1991, 33192/1991, 33193/1991), or fluorinated oil (see Japanese Patent Unexamined Publications No. 93896/1991).

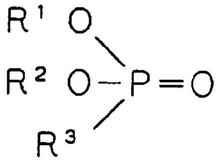
On the other hand, to prevent wear of metallic parts when HFC-134a is used as refrigerant, lubricating oil compositions blending various additives to the base oil have been proposed, but satisfactory results are not obtained yet.

It is hence keenly demanded in the lubricating oil composition for refrigerating machine using HFC-134a that the property of the composition itself to prevent wear of metallic parts (hereinafter called anti-wear property) should be improved so as to be equivalent or superior to the wear resistance of the conventional lubricating oil composition using CFC-12.

SUMMARY OF THE INVENTION

It is hence a primary object of the invention to present a lubricating oil composition for refrigerating machine using 1,1,1,2-tetrafluoroethane as refrigerant, being improved in anti-wear property.

To achieve the above object, the invention presents a lubricating oil composition for refrigerating machine comprising at least one organic phosphorus compound selected from a group comprising organic phosphonate expressed in Formula (I), organic phosphate expressed in Formula (V), and organic phosphate expressed in Formula (VI), out of polyalkylene glycol, ester base fluid , fluorinated oil and organic phosphorus compound as specified above, wherein, if composed of polyalkylene glycol and the organic phosphate expressed in Formula (V), the content of the organic phosphate in the base oil exceeds 10 wt.%.



(I)

where R^1, R^2 are either identical or different, expressing any one of the groups (1) to (4) below.

(1) an alkyl group with 1 to 18 carbon atoms,

(2) an alkenyl group with 3 to 18 carbon atoms,

(3) an aryl group with 6 to 18 carbon atoms (however, an alkyl group with 1 to 12 carbon atoms, or an alkenyl group with 2 to 12 carbon atoms may be possessed as a substitutent), and

(4) a polyoxyalkylene alkylether group expressed in Formula (II)

$$R^4O - (R^5O)_a - R^5 - \qquad (II)$$

(where R^4 denotes a hydrogen atom, an alkyl group with 1 to 18 carbon atoms, or an alkenyl group with 3 to 18 carbon atoms, R^5 represents an alkylene group with 2 to 4 carbon atoms, and a is 0 or an integer of 1 or more), and

R^3 denotes any one of the groups of (5) to (11):

(5) an alkyl group with 1 to 18 carbon atoms,

(6) an alkenyl group with 2 to 18 carbon atoms,

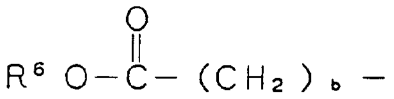
(7) an aryl group with 6 to 18 carbon atoms (an alkyl group with 1 to 12 carbon atoms or an alkenyl group with 2 to 12 carbon atoms may be possessed as a substituent),

(8) an polyoxyalkylene alkylether group expressed in Formula (IIa)

$$R^4O - (R^5O)_a - R^{21} - \qquad \text{(IIa)}$$

(where R^4, R^5 denote the same groups as above, R^{21} is an alkylene group with 1 to 4 carbon atoms, and a is the same integer as above),

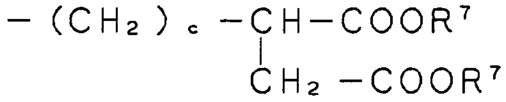
(9) a group expressed in Formula (III)



$$R^6 O-\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_b- \qquad \text{(III)}$$

[where R^6 denotes any one of an alkyl group with 1 to 18 carbon atoms, an alkenyl group with 3 to 18 carbon atoms, an aryl group with 6 to 18 carbon atoms (an alkyl group with 1 to 12 carbon atoms or an alkenyl group with 2 to 12 carbon atoms may be possessed as a substituent), and a polyoxyalkylene alkylether group expressed in Formula (II), and b is an integer from 1 to 3],

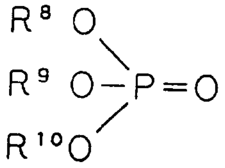
(10) a group expressed in Formula (IV)



$$-(CH_2)_c-\underset{\underset{\displaystyle CH_2-COOR^7}{|}}{C}H-COOR^7 \qquad \text{(IV)}$$

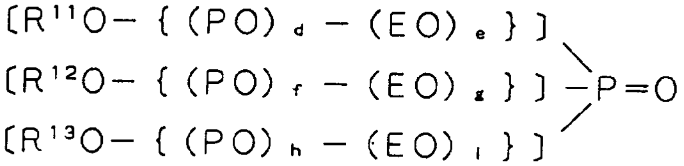
[where R^7 denotes any one of an alkyl group with 1 to 18 carbon atoms, an alkenyl group with 3 to 18 carbon atoms, an aryl group with 6 to 18 carbon atoms (an alkyl group with 1 to 12 carbon atoms or an alkenyl group with 2 to 12 carbon atoms may be possessed as a substituent), and a polyoxyalkylene alkylether group expressed in Formula (II), and c is 0 or 1], and

(11) a bezoyl group which may possess an alkyl group with 1 to 12 carbon atoms or an alkenyl group with 2 to 12 carbon atoms as a substituent



(V)

[where R^8, R^9, and R^{10} are either identical or different, expressing an alkyl group with 1 to 18 carbon atoms, or an alkenyl group with 3 to 18 carbon atoms],



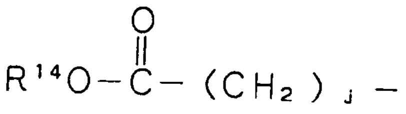
(VI)

[where R^{11}, R^{12}, and R^{13} are either identical or different, expressing any one of the groups (A) to (E) below, EO denotes an oxyethylene group, and PO represents an oxypropylene group; d to i denote 0 or integers of 1 or more, but d to i are not 0 at the same time; or when both d and e are integers of 1 or more, or when both f and g are integers of 1 or more, or when both h and i are integers of 1 or more, the oxyethylene group and oxypropylene group may be either bonded at random or bonded in block];

(A) an alkyl group with 1 to 18 carbon atoms,

(B) an alkenyl group with 3 to 18 carbon atoms,

(C) an aryl group with 6 to 18 carbon atoms (which may possess, however, either one of the groups, that is, an alkyl group with 1 to 12 carbon atoms, an alkenyl group with 2 to 12 carbon atoms, a group expressed in Formula (VII), or a group expressed in Formula (VIII), as a substituent),



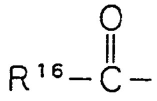
$$R^{14}O-\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_j- \qquad \text{(VII)}$$

(where R^{14} denotes an alkyl group with 1 to 18 carbon atoms, or an alkenyl group with 3 to 18 carbon atoms, and j is an integer from 2 to 15),

$$R^{15}O- \qquad \text{(VIII)}$$

(where R^{15} denotes an alkyl group with 1 to 8 carbon atoms, or an alkenyl group with 3 to 8 carbon atoms),

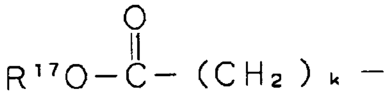
(D) a group expressed in Formula (IX),



$$R^{16}-\overset{\overset{\displaystyle O}{\|}}{C}- \qquad \text{(IX)}$$

[where R^{16} is an alkyl group with 1 to 18 carbon atoms, an alkenyl group with 2 to 18 carbon atoms, or an aryl group with 6 to 18 carbon atoms (which, however, may possess an alkyl group with 1 to 12 carbon atoms, or an alkenyl group with 2 to 12 carbon atoms as a substituent)], and

(E) a group expressed in Formula (X)



$$R^{17}O-\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_k- \qquad \text{(X)}$$

[where R^{17} is an alkyl group with 1 to 18 carbon atoms, an alkenyl group with 2 to 18 carbon atoms, or an aryl group with 6 to 18 carbon atoms (which, however, may possess either an alkyl group with 1 to 12 carbon atoms or an alkenyl group with 2 to 12 carbon atoms as a substituent), and k is an integer from 2 to 15.]

According to the investigations by the present inventors, the organic phosphonate expressed in Formula (I), the organic phosphate expressed in Formula (V), and the organic phosphate expressed in Formula (VI) may be all used as the base oil for the lubricating oil composition for refrigerating machine, and are all stable and compounds with excellent anti-wear property, and the lubricating oil composition for refrigerating machine using such compounds as the base oil is superior in antiwear property to the existing materials. In addition, these compounds are excellent in solubility with existing known base oils such as polyalkylene glycol, ester base fluid and fluorinated oil, and may be also used as antiwear agents for enhancing the anti-wear property of the base oils without adversely affecting the stability.

Therefore, the lubricating oil composition for refrigerating machine of the invention containing any one of the above compounds as the base oil or the additive (antiwear agent) for the known base oil exhibits, by itself, an excellent anti-wear property superior to that of the existing lubricating oil composition using CFC-12, and therefore it improves the anti-wear property of the system using HFC-134a not acting as extreme-pressure agent as refrigerant, and hence extremely reduces the wear of metallic parts exposed inside the compressor. Moreover, its anti-wear property is extremely excellent as compared with the anti-wear property of the lubricating oil composition for refrigerating machine using CFC-12 as refrigerant.

DETAILED DESCRIPTION OF THE INVENTION

Practical examples of the organic phosphonate expressed in Formula (I) include the following compounds.

O,O-dimethyl oleylphosphonate, O,O-dimethyl stearylphosphonate, O,O-dimethyl n-octylphosphonate, O,O-dimethyl 2-ethylhexylphosphonate, O,O-diethyl oleylphosphonate, O,O-diethyl laurylphosphonate, O,O-diethyl n-octylphosphonate, O,O-diethyl 2-ethylhexylphosphonate, O,O-diisopropyl oleylphosphonate, O,O-diisopropyl stearylphosphonate, O,O-diisopropyl n-octylphosphonate, O,O-diisopropyl 2-ethylhexylphosphonate, O,O-di-n-butyl oleylphosphonate, O,O-di-n-butyl laurylphosphonate, O,O-di-n-butyl n-octylphosphonate, O,O-di-n-butyl 2-ethylhexylphosphonate, O,O-di-n-butyl hexylphosphonate, O,O-di-n-butyl decylphosphonate, 0,0-di-2-ethylhexyl oleylphosphonate, 0,0-di-2-ethylhexyl stearylphosphonate, 0,0-di-2-ethylhexyl laurylphosphonate, 0,0-di-2-ethylhexyl n-octylphosphonate, 0,0-di-2-ethylhexyl hexylphosphonate, 0,0-di-2-ethylhexyl n-butylphosphonate, 0,0-di-2-ethylhexyl tris(ethyleneglycol)methylenephosphonate, 0,0-di-2-ethylhexyl isooctylphosphonate, O,O-diisocotyl oleylphosphonate, O,O-diisooctyl laurylphosphonate, O,O-diisooctyl n-octylphosphonate, O,O-diisooctyl 2-ethylhexylphosphonate, O,O-diisooctyl hexylphosphonate, O,O-diisooctyl n-butylphosphonate, O,O-diisooctyl decylphosphonate, O,O-di-n-octyl isooctylphosphonate, O,O-di-n-octyl 2-ethylexylphosphonate, O,O-di-n-octyl oleylphosphonate, O,O-di-n-octyl hexylphosphonate, O,O-diisodecyl stearylphosphonate, O,O-diisodecyl laurylphosphonate, O,O-diisodecyl isodecylphosphonate, O,O-diisodecyln-octylphosphonate, O,O-diisodecyl 2-ethylhexylphosphonate, O,O-diisodecyl hexylphosphonate, O,O-diisodecyln-butylphosphonate, O,O-diisodecyl methylphosphonate, O,O-dilauryl decylphosphonate, O,O-dilauryl 2-ethylhexylphosphonate, O,O-dilauryl n-octylphosphonate, O,O-dilauryl hexylphosphonate, O,O-dilauryl n-butylphosphonate, O,O-dilauryl methylphosphonate, O,O-dioleyl decylphosphonate, O,O-dioleyl 2-ethylhexylphosphonate, O,O-dioleyl n-octylphosphonate, O,O-dioleyl hexylphosphonate, O,O-dioleyl n-butylphosphonate, O,O-dioleyl isobutylphosphonate, O,O-dioleyl methylphosphonate, O,O-di-2-ethylhexyl phenylphosphonate, O,O-diisooctyl phenylphosphonate, O,O-di-2-ethylheyl 3,5-di-t-butyl-4-hydroxybenzylphosphonate, O,O-didecyl 3,5-di-t-butyl-4-hydroxybenzylphosphonate, O,O-diethyl benzylphosphonate, O,O-diethyl 4-methylbenzylphosphonate, O,O-diethyl p-hydroxybenzylphosphonate, O,O-diethyl 3,5-dimethylbenzylphosphonate, O,O-diethyl p-methoxybenzylphosphonate, O,O,O,O-tetraethyl[1,4-phenylenebis(methylene)]phosphonate, O,O-di-s-butyl 3,5-di-t-butyl-4-hydorxyphenylphosphonate, O,O-dimethylphosphonomethylene(dimethyl)succinate, O,O-dimethylphosphonomethylene(di-2-ethylhexyl)succinate, O,O-di-2-ethylhexylphosphonomethylene(dimethyl)succinate, O,O-di-2-ethylhexylphosphonomethylene(dibutyl)succinate, O,O-didecylphosphonomethylene(dimethyl) succinate, O,O-di-2-ethylhexyl-3-phosphonomethyl propionate, O,O-diisohexyl-3-phosphonobutyl propionate, O,O-di-2-ethylhexyl-3-phosphono-2-ethylhexyl propionate, O,O-diphenyl 2-ethylhexylphosphonate, O,O-diphenyl phenylhexylphosphonate, O,O-dihexyl hexylphosphonate, O,O-di-2-ethylhexyl 2-ethylhexylphosphonate, O,O-diisooctyl isooctylphosphonate, O,O-di-n-octyl n-octylphosphonate, O,O-didecyl decylphosphonate, O,O-dilauryl laurylphosphonate, O,O-di(decylpolyoxyethylene) (decylpolyoxyethylene)phosphonate, O,O-di(butyloxyethylene) (butyloxyethylene)phosphonate, O-butyl-O-2-ethylhexyl 2-ethylyhexylphosphonate, O-decyl-O-2-ethylhexyl 2-ethylhexylphosphonate, O,O-di-2-ethylhexyl phosphonomethylene polyethylene glycol, O,O-di-2-ethylhexyl phosphonodimethyl succinate, O,O-di-2-ethylhexyl phenylcarbonylphosphonate, and O,O-dibutyl p-methylphenylcarbonylphosphonate.

The organic phosphonates presented above may be prepared by known methods. For example, O,O-diisooctyl isooctylphosphonate may be prepared by reaction of triisooctyl phosphite and isooctyl bromide.

The content of the organic phosphonate in the base oil is not particularly defined in the invention. As stated above, since the organic phosphonate can be used not only as the base oil but also as the additive (anti-wear agent) for other base oil, and its content may be arbitrary including 100 wt.% (that is, the whole base oil may be an organic phosphonate). Preferably, the content should be 0.01 wt.% or more. If the content of the organic phosphonate is less than 0.01 wt.%, its additive effect is insufficient, and sufficient anti-wear property may not be achieved. As other base oil to be used together with the organic phosphonate, known base oils such as polyalkylene glycol, ester base fluid and fluorinated oil, and organic phosphate expressed in Formula (V) or (VI) may be used.

Practical examples of the organic phosphate expressed in Formula (V) include the following compounds.

Dimethyloleyl phosphate, dimethyltridecyl phosphate, dimethyllauryl phosphate, di-n-butyltridecyl phosphate, di-n-butyldodecyl phosphate, di-n-butyl-2-ethylhexyl phosphate, di-2-ethylhexyltridecyl phosphate, di-2-ethylhexyldodecyl phosphate, di-2-ethylhexyl-n-octyl phosphate, di-2-ethylhexyldecyl phosphate, di-2-ethylhexylisooctyl phosphate, diisooctyl-2-ethylhexyl phosphate, diisooctyl-n-octyl phosphate, di-n-octyl-2-ethylhexyl phosphate, di-n-octylisooctyl phosphate, di-2-ethylhexylhexyl phosphate, di-2-ethylhexyl-n-butyl phosphate, di-2-ethylhexylallyl phosphate, diisooctyldodecyl phosphate, diisooctyldecyl phosphate, diisooctylhexyl phosphate, diisooctyl-n-butyl phosphate, di-n-octyldodecyl phosphate, di-n-octyldecyl phosphate, di-n-octylhexyl phosphate, didecyldodecyl phosphate, didecyl-2-ethylhexyl phosphate, didecylisooctyl phosphate, didecyl-n-octyl phosphate, didecyl-n-butyl phosphate, didodecyl-2-ethylhexyl phosphate, didodecylhexyl phosphate, didodecyl-n-butyl phosphate, didodecylmethyl phosphate, tris(2-ethylhexyl) phosphate, tris(isooctyl)phosphate, tris(n-octyl)phosphate, tris(decyl)phosphate, tris(dodecyl)phosphate, and tris(hexyl)phosphate.

The examples of organic phosphate may be prepared by known methods. For example tris(2-ethylhexyl)phosphate may be prepared by the reaction of 2-ethylhexanol and phosphorus oxychloride in the presence of dehydrohalogenating agent.

Other base oils to be used together with the organic phosphate include known base oils such as polyalkylene glycol, ester base fluid and fluorinated oil, organic phosphonate expressed in Formula (I), and organic phosphate expressed in Formula (VI).

When the lubricating oil composition for refrigerating machine of the invention is substantially composed of the organic phosphate expressed in Formula (V) and polyalkylene glycol, the rate of the organic phosphate in the base oil must exceed 10 wt.%. The polyalkylene glycol is high in moisture absorption rate, and it may absorb more than 1.0% of moisture, which may adversely affect the stability of the lubricating oil composition for refrigerating machine. It is accordingly necessary to increase the content of the organic phosphate which does not absorb moisture so as to lower the moisture content of the entire composition, and hence the content of the organic phosphate is limited in a range exceeding 10 wt.%. Moreover, when the organic phosphate expressed in Formula (V) is blended by more than 10 wt.%, it is also effective to suppress the temperature of the sliding surface, which further contributes to decrease of decomposition of refrigerant (enhancement of stability).

Otherwise, the content of the organic phosphate expressed in Formula (V) in the base oil is desired to be 0.01 wt.% or more, owing to the same reason as in the case of organic phosphonate.

The upper limit of content of the organic phosphate is, in any case above, is 100 wt.% same as in the case of organic phosphonate mentioned above.

Practical examples of organic phosphate expressed in Formula (VI) include the following compounds.

Tris(tridecyloxyethylene)phosphate, tris[poly(oxyethylene)tridecyl]phosphate, tris(decyloxyethylene)phosphate, tris[poly(oxyethylene)decyl]phosphate, tris(2-ethylhexyloxyethylene)phosphate, tris[poly(oxyethylene)-2-ethylhexyl]phosphate, tris(isooctyloxyethylene)phosphate, tris[poly(oxyethylene)isooctyl]phosphate, tris(n-octyloxyethylene)phosphate, tris[poly(oxyethylene)-n-octyl]phosphate, tris(n-butyloxyethylene)phosphate, tris [poly(oxyethylene)-n-butyl]phosphate, bis[poly(oxyethylene)-2-ethylhexyl][poly(oxyethylene)-iso-octyl]phosphate, di[poly(oxyethylene)-n-octyl][poly(oxyethylene)-2-ethylhexyl]phosphate, bis[poly(oxyethylene)-2-ethylhexyl-][poly(oxyethylene)decyl]phosphate, tris[poly(oxyethylene)-poly(oxypropylene)-2-ethylhexyl]phosphate, tris[poly (oxyethylene)propyleneoxy-2-ethylhexyl]phosphate, tris[ethyleneoxy-poly(oxypropylene)-isooctyl]phosphate, tris[ethyleneoxy-poly(oxypropylene)-n-octyl]phosphate, tris[poly(oxyethylene)-poly(oxypropylene)-n-octyl]phosphate, di[poly(oxyethylene)-n-butyl][poly(oxyethylene)oleyl]phosphate, tris[poly(oxyethylene)carbonylpropyl] phosphate, tris(ethylenebutylate)phosphate, tris(ethylene-2-etylhexanoate)phosphate, tris[poly(oxyethylene) carbonyl-1-ethyl-pentyl]phosphate, tris[poly(oxyethylene)carbonylundecyl]phosphate, tris[poly(oxyethylene) propyleneoxycarbonyl-1-ethylpentyl]phosphate, tris[poly(oxyethylene)poly(oxypropylene)carbonyl-1-ethylpentyl]phosphate, tris[poly(oxyethylene)propyleneoxycarbonyl-1-methylvinyl]phosphate, tris[3-poly(oxyethylene)-methyl-2-methylpropionate]phosphate, tris[poly(oxyethylene)-2-hydroxyoctyl]phosphate, tris(p-octylphenoxyethylene)phosphate, tris[poly(oxyethylene)-p-octylphenyl]phosphate, tris[poly(oxyethylene)-poly(oxypropylene)-p-methylphenoxy]phosphate, tris[4-poly(oxyethylene)ethylphenylacetate]phosphate, tris[poly(oxyethylene) poly(oxypropylene)-p-butoxyphenyl]phosphate, bis[poly(oxyethylene)-2-ethylhexyl](2-ethylenehexyl)phosphate, bis (2-ethylhexyl)[poly(oxyethylene)-2-ethylhexyl]phosphate, bis(2-ethylhexyl)[poly(oxyethylene)tridecyl]phosphate, bis(2-ethylhexyl)[poly(oxyethylene)alkyl]phosphate [of which alkyl group is a secondary alkyl group with 11 to 15 carbon atoms], and bis(2-ethylhexyl)[poly(oxyethylene)poly(oxypropylene)alkyl]phosphate [of which alkyl group is an alkyl group with 6 to 10 carbon atoms].

These examples of organic phosphate may be prepared by known methods. For examples, tris[di(oxyethylene)-2-ethylhexyl]phosphate is prepared by the reaction of phosphorus oxychloride and dioxyethylene-2-ethylhexylether in the presence of dehydrohalogenating agent.

The content of the organic phosphate in the base oil is, same as specified above, desired to be in a range of 0.01 to 100 wt.%. Other base oils to be used together with the organic phosphate may include known base oils such as polyalkylene glycol, ester base fluid and fluorinated oil, organic phosphonate expressed in Formula (I), and organic phosphate expressed in Formula (V).

As the polyalkylene glycol to be used together with any one of the organic phosphonate expressed in Formula (I), the organic phosphate expressed in Formula (V), and the organic phosphate expressed in Formula (VI), various known polyalkylene glycols may be used, and in particular, the compound expressed in Formula (XI) is desired.

$$A^1 - [O - (EO)_m - (PO)_n - A^2]_p \qquad (XI)$$

where EO denotes an oxyethylene group, and PO is an oxypropylene group; m and n are 0 or integers of 1 or more, but m and n are not 0 at the same time; if m and n are both integers of 1 or more, the oxyethylene group and oxypropylene group may be bonded either at random or in block; the ratio of m and m, m/n, is desired to be 1 or less; and p is an integer of 1 to 4.

If p is 1, A^1 is any one of the following:

(a) a hydrogen,

(b) an alkyl group with 1 to 18 carbon atoms,

(c) an alkenyl group with 3 to 18 carbon atoms, or

(d) an aryl group with 6 to 18 carbon atoms (which may possess either an alkyl group with 1 to 12 carbon atoms or an alkenyl group with 2 to 12 carbon atoms as a substituent).

If p is 2, A^1 represents a residue by removing hydroxy group from dihydroxy compound. In particular, a residue by removing hydroxy group from saturated aliphatic dihydroxy compound, unsaturated aliphatic dihydroxy compound, or aromatic dihydroxy compound is preferably used, such as ethylene glycol and propylene glycol.

If p is 3, A^1 represents a residue by removing hydroxy group from trihydroxy compound. In particular, a residue by removing hydroxy group from saturated aliphatic trihydroxy compound, unsaturated aliphatic trihydroxy compound, or aromatic trihydroxy compound is preferably used, such as gylcerin and trimethylolpropane.

If p is 4, A^1 represents a residue by removing hydroxy group from tetrahydroxy compound. In particular, a residue by removing hydroxy group from saturated aliphatic tetrahydroxy compound, or unsaturated aliphatic tetrahydroxy compound is preferably used, such as pentaerythritol.

In Formula (XI), A^2 represents one of the following:

(e) a hydrogen,

(f) an alkyl group with 1 to 20 carbon atoms,

(g) an alkenyl group with 3 to 20 carbon atoms,

(h) an aryl group with 6 to 18 carbon atoms (which may possess either alkyl group with 1 to 12 carbon atoms or alkenyl group with 2 to 12 carbon atoms as a substituent), or

(i) an acyl group expressed in Formula (XII)

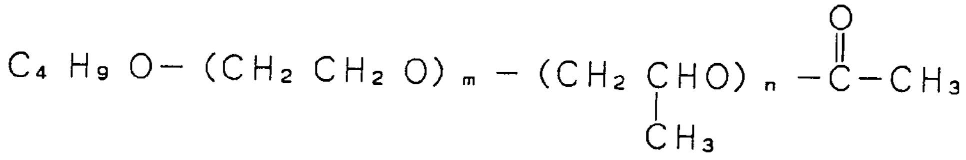
$$- CO - A^3 \qquad (XIII)$$

where A^3 represents any one of alkyl group with 1 to 17 carbon atoms, alkenyl group with 3 to 17 carbon atoms, and aryl group with 6 to 18 carbon atoms (which may possess either alkyl group with 1 to 12 carbon atoms or alkenyl group with 2 to 12 carbon atoms as a substituent).

Meanwhile, in the combined system with the organic phosphonate expressed in Formula (I), if p is 1, A^1 and A^2 in Formula (XI) are not hydrogen at the same time, and if p is 2 to 4, two or more of A^2 are not hydrogen at the same time.

The kinematic viscosity at 40 deg. C of polyalkylene glycol expressed in Formula (XI) is desired to be in a range of 5 to 300 cSt. If the kinematic viscosity is less than 5 cSt, the lubricating performance as the base oil including anti-wear property is not sufficient, and if exceeding 300 cSt, the solubility may be inferior. More preferably, the kinematic viscosity of polyalkylene glycol at 40 deg. C should be in a range of 15 to 150 cSt.

Practical examples of polyalkylene glycol expressed in Formula (XI) may include compounds expressed in Formula (XIII), of which kinematic viscosity at 40 deg. C is 32 cSt.



$$C_4H_9O-(CH_2CH_2O)_m-(CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HO)_n-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3$$

(XIII)

where m and n are integers of which ratio m/n is 0.6

As the ester base fluid used together with the base oil, various hitherto known ester base fluids may be used, and in particular the oils expressed in Formula (XIV) are used preferably.

$$A^4 - (OCOA^5)_q \qquad (XIV)$$

where q denotes an integer of 1 to 4.

If q is 1, A^4 represents any one of the following:

(j) an alkyl group with 1 to 18 carbon atoms,

(k) an alkenyl group with 3 to 18 carbon atoms, or

(l) an aryl group with 6 to 18 carbon atoms (which may possess either alkyl group with 1 to 12 carbon atoms or alkenyl group with 2 to 12 carbon atoms as a substituent).

If q is 2, A^4 represents a residue by removing hydroxy group from dihydroxy compound. In particular, a residue by removing hydroxy group from saturated aliphatic dihydroxy compound, unsaturated aliphatic dihydroxy compound, or aromatic dihydroxy compound is preferably used, such as ethylene glycol and propylene glycol.

If q is 3, A^4 represents a residue by removing hydroxy group from trihydroxy compound. In particular, a residue by removing hydroxy group from saturated aliphatic trihydroxy compound, unsaturated aliphatic trihydroxy compound, or aromatic trihydroxy compound is preferably used, such as gylcerin and trimethylolpropane.

If q is 4, A^4 represents a residue by removing hydroxy group from tetrahydroxy compound. In particular, a residue by removing hydroxy group from saturated aliphatic tetrahydroxy compound, or unsaturated aliphatic tetrahydroxy compound is preferably used, such as pentaerythritol.

In particular, alkyl group or alkenyl group not possessing hydrogen in β -carbon is desired.

In Formula (XIV), A^5 represents one of the following:

(m) an alkyl group with 1 to 17 carbon atoms,
(n) an alkenyl group with 3 to 17 carbon atoms, or
(o) an aryl group with 6 to 18 carbon atoms (which may possess either alkyl group with 1 to 12 carbon atoms or alkenyl group with 2 to 12 carbon atoms as a substituent).

Practical examples of ester base fluid expressed in Formula (XIV) include, among others, octyl oleate, trimethylol propane triheptanoate, and pentaerythritol tetraoctanoate.

As other ester base fluids than mentioned above, for example, diester dicorboxylate expressed in Formula (XV) may be used.

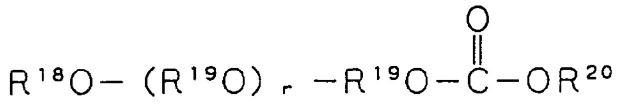
$$A^6 - (COOA^7)_2 \qquad (XV)$$

where A^6 represents one of the following:

(p) an alkyl group with 1 to 18 carbon atoms,
(q) an alkenyl group with 3 to 18 carbon atoms, or
(r) an aryl group with 6 to 18 carbon atoms (which may possess either alkyl group with 1 to 12 carbon atoms or alkenyl group with 2 to 12 carbon atoms as a substituent), and A^7 represents one of the following:
(s) an alkyl group with 3 to 18 carbon atoms,
(t) an alkenyl group with 3 to 18 carbon atoms, or
(u) an aryl group with 6 to 18 carbon atoms (which may possess either alkyl group with 1 to 12 carbon atoms or alkenyl group with 2 to 12 carbon atoms as a substituent), or
(v) a polyoxyalkylene alkylether group expressed in Formula (II).

The dicarboxylic acid as the material for the diester dicarboxylate may include, for example, succinic acid, adipic acid, azelaic acid, sebacic acid, phthalic acid, isophthalic acid, terephthalic acid, tetradecanoic diacid, and hexadecanoic diacid, and practical examples of ester base fluid expressed in Formula (XV) include, among others, 1,9-azelaic dioctyl ester, 1,14-tetradecanoic dioctyl ester, and 1,16-hexadecanoic dioctyl ester.

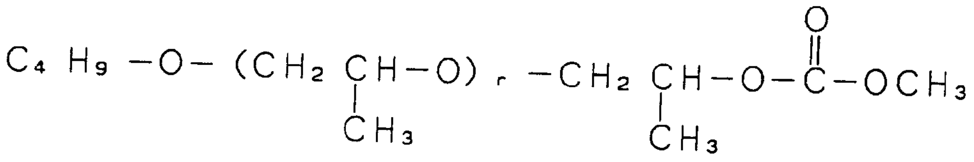
As other ester base fluid, the carbonate ester expressed in Formula (XVI) may be known, for example.



$$R^{18}O-(R^{19}O)_r-R^{19}O-\overset{\overset{\displaystyle O}{\|}}{C}-OR^{20} \qquad (XVI)$$

where R^{18}, R^{20} are identical or different, representing alkyl group with 1 to 18 carbon atoms, alkenyl group with 3 to 18 carbon atoms, or aryl group with 6 to 18 carbon atoms (which may possess either alkyl group with 1 to 12 carbon atoms or alkenyl group with 2 to 12 carbon atoms as a substituent), R^{19} represents an alkylene group with 2 to 4 carbon atoms, and r is 0 or an integer of 1 or more.

A practical example of carbonate ester includes a compound of which kinematic viscosity at 40 deg. C is 32 cSt as expressed-in Formula (XVIa):



$$C_4H_9-O-(CH_2\underset{\underset{\displaystyle CH_3}{|}}{C}H-O)_r-CH_2\underset{\underset{\displaystyle CH_3}{|}}{C}H-O-\overset{\overset{\displaystyle O}{\|}}{C}-OCH_3 \qquad (XVIa)$$

where C_4H_9 is an n-buty group.

The ester base fluid explained herein is desired to have the kinematic viscosity at 40 deg. C in a range of

5 to 300 cSt, especially in a range of 15 to 60 cSt, considering its use in refrigerating machine.

The fluorinated oil used together with the base oil includes various known fluorinated oils, and in particular the compound in Formula (XVII) is desired.

$$A^8 - [O - (C_sF_{2s})_t - C_uF_{2u}\text{-}OA^9]_v \qquad \text{(XVII)}$$

where A^8 denotes a perfluoroalkyl group with 1 to 12 carbon atoms, A^9 represents a perfluoroalkyl group with 1 to 4 carbon atoms or an acyl group expressed in Formula (XVIII), s is an integer of 1 to 4, t is an integer of 1 or more, and u and v are either identical or different, representing integers of 1 to 3.

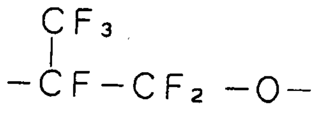
$$\text{-CO-}A^{10} \qquad \text{(XVIII)}$$

where A^{10} denotes a perfluoroalkyl group with 1 to 4 carbon atoms.

A practical example of such fluorinated oil includes a compound expressed in Formula (XIX).

$$C_4F_9O - (C_2F_4O)_4 - C_2F_4O - CF_3 \qquad \text{(XIX)}$$

Besides, the fluorinated oil consisting of a constituent unit expressed in Formula (XX).



$$-\overset{\overset{\displaystyle CF_3}{|}}{C}F-CF_2-O- \qquad \text{(XX)}$$

may be also preferably used in the invention

Generally, if the acid value of the lubricating oil composition for refrigerating machine is too high, the stability is lowered, which may induce corrosion of metal and adverse effects on anti-wear property Therefore, the acid value should be as low as possible, and in particular it is desired to be 0.01 [mg KOH/g] or less.

In the lubricating oil composition for refrigerating machine, usually, aromatic phosphate or the like is used as extreme-pressure agent, but when its content increases, it may adversely affect the stability. However, in the lubricating oil composition for refrigerating machine of the invention, if the content of the organic phosphorus compound expressed in Formula (I), (V) or (VI) is increased, the anti-wear property is enhanced without impairing the stability.

Accordingly, in the lubricating oil composition for refrigerating machine of the invention, the ordinary additive added conventionally to the lubricating oil composition may be added by the conventional blending rate.

Such additives may include, for example, an epoxy compounds for stabilizing the lubricating oil composition. Practical examples of epoxy compounds are, among others, condensate of polyalkylene glycol and epichlorohydrine, condensate of phenol and glycidyl alcohol, and epoxy fatty ester.

The epoxy compounds are usually blended to the base oil in a range of 0.1 to 10 wt.%. If the content of the epoxy compounds are less than the specified range, the effect of adding the epoxy compounds are insufficient, or, to the contrary, if the blending of the epoxy compounds are more than the range, it may be harmful for the antiwear property of the lubricating oil composition.

Other additives than the stabilizer may include antioxidant of phenol and amine compounds, oilness of sulfur compounds, metal deactivator of benzotriazole compounds.

The lubricating oil composition for refrigerating machine of the invention is prepared by adding, as required, polyalkylene glycol, ester base fluid, fluorinated oil, or other base oils, and various additives to the organic phosphonate expressed in Formula (I), organic phosphate expressed in Formula (V), or organic phosphate expressed in Formula (VI), and agitating and dissolving at room temperature to 80 deg. C, or preferably, room temperature to 40 deg. C.

The lubricating oil composition for refrigerating machine of the invention is preferably used in the refrigerating machine such as refrigerator, car cooler, freezer, and refrigerated display case incorporating a compressor of rotary type, reciprocating type, centrifugal type or the like.

EXAMPLES

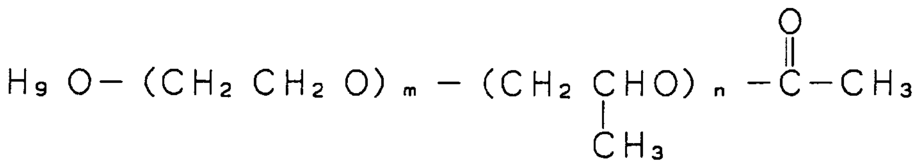
The invention is specifically described below while referring to some of the preferred examples thereof, but it must be noted that the invention is not limited to these examples alone.

Examples 1 to 40

An organic phosphonate of which R^1 to R^3 expressed in Formula (I) are substituents shown in Tables 1 to 4 below was blended with a base oil shown in the same tables, dissolved uniformly, and lubricating oil compositions for refrigerating machine of Examples 1 to 40 were prepared. The blending rate of organic phosphonate in the base oil was 1.0 wt.%

In the base oil columns of Tables 1 to 4, the symbols P, E, F, V represent the following compounds, respectively.

P: Polyalkylene glycol expressed in Formula (XIII), of which kinematic viscosity at 40 deg. C is 32 cSt.



$$H_9O-(CH_2CH_2O)_m-(CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HO)_n-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3 \qquad (XIII)$$

where m and n are integers of which ratio m/n is 0.6.

E: Pentaerythritol tetraoctanoate as ester base fluid.

F: Fluorinated oil expressed in Formula (XIX).

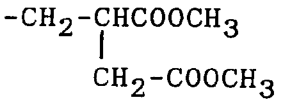
$$C_4F_9O - (C_2F_4O)_4 - C_2F_4O - CF_3 \qquad (XIX)$$

V: Organic phosphate of which R^8, R^9, R^{10} are commonly 2-ethylhexyl groups.

In the column of organic phosphonate, the symbols represent the following substituents, respectively.

M	methyl group
DD	dodecyl group
Et	ethyl group
nB	n-butyl group
D	decyl group
EH	2-ethylhexyl group
iO	isooctyl group
nO	n-octyl group
OD	octadecyl group
ϕ	phenyl group
nH	n-hexyl group

(1)



$$-CH_2-\underset{\displaystyle CH_2-COOCH_3}{\underset{|}{C}}HCOOCH_3$$

(2) $-CH_2-CH_2-COOCH_3$

(3) $-CH_2-(OC_2H_4)_3-OH$

(4) $C_{10}H_{21}O-C_2H_4O-C_2H_4-$

(5) $-CH_2-OH$

Comparative Example 1

Only the polyalkylene glycol expressed in Formula (XIII) as the base oil was used as the lubricating oil composition for refrigerating machine of Comparative Example 1.

Comparative Example 2

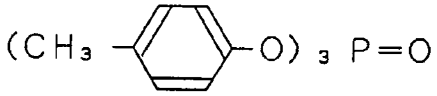
Only the pentaerythritol tetraoctanoate as the base oil was used as the lubricating oil composition for refrigerating machine of Comparative Example 2.

Comparative Example 3

Only the fluorinated oil expressed in Formula (XIX) as the base oil was used as the lubricating oil composition for refrigerating machine of Comparative Example 3.

Comparative Example 4

The aromatic phosphate expressed below was blended with polyalkylene glycol as base oil expressed in Formula (XIII), and dissolved uniformly to prepare the lubricating oil composition for refrigerating machine of Comparative Example 4. The blending rate of aromatic phosphate in the base oil was 1.0 wt.%.



Comparative Example 5

The same aromatic phosphate as in Comparative Example 4 was blended with pentaerythritol tetraoctanoate as base oil, and dissolved uniformly to prepare the lubricating oil composition for refrigerating machine of Comparative Example 5. The blending rate of aromatic phosphate in the base oil was 1.0 wt.%.

Comparative Example 6

The compound expressed below was blended with pentaerythritol tetraoctanoate as base oil, and dissolved uniformly to prepare the lubricating oil composition for refrigerating machine of Comparative Example 6. The blending rate of the compound in the base oil was 1.0 wt.%.

$$(C_{18}H_{35}0)_2P(O)H$$

Comparative Example 7

The phosphate expressed below was blended with pentaerythritol tetraoctanoate as base oil, and dissolved uniformly to prepare the lubricating oil composition for refrigerating machine of Comparative Example 7. The blending rate of phosphate in the base oil was 1.0 wt.%.

$$(C_{18}H_{35}0)_3\text{-}P = O$$

Comparative Example 8

The compound expressed below was blended with pentaerythritol tetraoctanoate as base oil, and dissolved uniformly to prepare the lubricating oil composition for refrigerating machine of Comparative Example 8. The blending rate of-the compound in the base oil was 1.0 wt.%.

$$(C_{18}H_{35}0)_3\text{-}P$$

Comparative Example 9

The compound expressed below was blended with pentaerythritol tetraoctanoate as base oil, and dissolved uniformly to prepare the lubricating oil composition for refrigerating machine of Comparative Example 9. The blending rate of the compound in the base oil was 1.0 wt.%.

$$(C_4H_90)_3\text{-}P = O$$

On the lubricating oil compositions for refrigerating machine of these Examples and Comparative Examples, the following tests were conducted.

Wear test

Evaluated by using Falex testing machine. At the rotating speed of 290 rpm, while blowing in HFC-134a at a flow rate of 5 liters/hour, the test was conducted for 1 hour at a load of 300 lbs, and the total wear of pins and V-blocks was measured. The result was expressed as relative value (wear ratio), regarding the amount of wear by using CFC-12 as refrigerant and mineral oil as base oil to be 1.

Mutual solubility test

The lubricating oil compositions for refrigerating machines of the Examples and Comparative Examples were dissolved in HFC-134a as refrigerant at the blending rates of 3 wt.%, 10 wt.%, 50 wt.% as calculated in the formula below. The solution was poured in a glass tube which was sealed tightly, and cooled to -50 deg. C, and presence or absence of separation of solution was observed. It was evaluated as O if not separated at -50 deg. C, and X if separated before reaching -50 deg. C.

$$\text{Blend (wt.\%)} = \frac{X\,(g)}{X\,(g) + Y\,(g)} X100$$

where

X: weight of lubricating oil composition
Y: weight of HFC-134a

Stability test

Evaluated by sealed tube test. Sampling 1 g each from the lubricating oil compositions for refrigerating machine in the Examples and Comparative Examples and from HFC-134a, three pieces of metal catalysts, that is, iron, copper and aluminum, were sealed in and enclosed. After heating at 175 deg. C for 14 days, the appearance of metal catalysts was observed. It was evaluated as ○ when no abnormality was detected, Δ if slightly discolored, and x if extremely discolored.

The results of measurement of the Examples are shown in Tables 1 to 4, and those of the Comparative Examples in Table 5.

Table 1

Example No.	base oil	substituents of organic phosphonate			anti-wear property (wear ratio)	solubility (−50℃)			stability		
		R^1	R^2	R^3		3%	10%	50%	Fe	Cu	Al
1	E	M	M	DD	0.3	○	○	○	○	○	○
2	P	Et	Et	DD	0.2	○	○	○	○	○	○
3	E	nB	nB	D	0.1	○	○	○	○	○	○
4	P	EH	EH	DD	0	○	○	○	○	○	○
5	P	EH	EH	EH	0	○	○	○	○	○	○
6	E	EH	EH	EH	0	○	○	○	○	○	○
7	F	EH	EH	EH	0	○	○	○	○	○	○
8	P	EH	EH	iO	0	○	○	○	○	○	○
9	E	EH	EH	iO	0	○	○	○	○	○	○
10	E	EH	EH	nB	0	○	○	○	○	○	○

Table 2

Example No.	base oil	substituents of organic phosphonate			anti-wear property (wear ratio)	solubility (−50℃)			stability		
		R^1	R^2	R^3		3%	10%	50%	Fe	Cu	Al
11	P	iO	iO	iO	0	○	○	○	○	○	○
12	E	iO	iO	iO	0	○	○	○	○	○	○
13	F	iO	iO	iO	0	○	○	○	○	○	○
14	P	iO	iO	EH	0	○	○	○	○	○	○
15	E	iO	iO	EH	0	○	○	○	○	○	○
16	E	iO	iO	D	0	○	○	○	○	○	○
17	P	nO	nO	nO	0	○	○	○	○	○	○
18	E	D	D	EH	0	○	○	○	○	○	○
19	P	DD	DD	D	0	○	○	○	○	○	○
20	E	DD	DD	EH	0	○	○	○	○	○	○

Table 3

Example No.	base oil	substituents of organic phosphonate			anti-wear property (wear ratio)	solubility (−50℃)			stability		
		R^1	R^2	R^3		3%	10%	50%	Fe	Cu	Al
21	P	DD	DD	M	0.2	○	○	○	○	○	○
22	E	OD	OD	nB	0	○	○	○	○	○	○
23	P	EH	EH	φ	0	○	○	○	○	○	○
24	E	EH	EH	φ	0	○	○	○	○	○	○
25	P	M	M	(1)	0.2	○	○	○	○	○	○
26	E	M	M	(1)	1.1	○	○	○	○	○	○
27	E	EH	EH	(1)	0.3	○	○	○	○	○	○
28	P	EH	EH	(2)	0.7	○	○	○	○	○	○
29	P	EH	EH	(3)	0.2	○	○	○	○	○	○
30	E	EH	EH	(3)	0.3	○	○	○	○	○	○

Table 4

Example No.	base oil	substituents of organic phosphonate			anti-wear property (wear ratio)	solubility (−50°C)			stability		
		R^1	R^2	R^3		3%	10%	50%	Fe	Cu	Al
31	P	nH	nH	nH	0.3	○	○	○	○	○	○
32	E	nH	nH	nH	0.2	○	○	○	○	○	○
33	P	D	D	D	0	○	○	○	○	○	○
34	E	(4)	(4)	(4)	0	○	○	○	○	○	○
35	E	EH	EH	nO	0	○	○	○	○	○	○
36	E	nO	nO	EH	0	○	○	○	○	○	○
37	E	nO	nO	iO	0	○	○	○	○	○	○
38	E	iO	iO	nO	0	○	○	○	○	○	○
39	E	EH	EH	(5)	0	○	○	○	○	○	○
40	V	EH	EH	EH	0	○	○	○	○	○	○

Table 5

Comparative Example No.	anti-wear property (wear ratio)	solubility (−50℃)			stability		
		3%	10%	50%	Fe	Cu	Al
1	2.3	−	−	−	○	○	○
2	1.5	−	−	−	△	○	○
3	2.0	−	−	−	○	○	○
4	2.3	○	○	○	○	○	○
5	1.5	○	○	○	○	○	○
6	1.2	○	○	○	×	×	×
7	−	×	×	×	−	−	−
8	−	○	×	○	×	×	×
9	2.0	○	○	○	○	○	○

It is known from these tables that the lubricating oil compositions for refrigerating machine in Comparative Examples 1 to 3 not containing organic phosphonate were all inferior in anti-wear property. The lubricating oil compositions for refrigerating machine of Comparative Examples 4, 5, 9 were also found to be inferior in anti-wear property. The lubricating oil composition for refrigerating machine of the Comparative Example 6 was discovered to be inferior in both anti-wear property and stability. Furthermore, the lubricating oil composition for refrigerating machine of Comparative Example 7 was known to be inferior in solubility, and the lubricating oil composition for refrigerating machine of Comparative Example 8 was found to be inferior in both solubility and stability.

By contrast, the lubricating oil compositions for refrigerating machine of Examples 1 to 40 were all found to be excellent in anti-wear property, solubility, and stability.

Examples 41 to 49

The organic phosphonate of which R^1 to R^3 in Formula (I) are commonly 2-ethylhexyl groups, and polyalkylene glycol expressed in Formula (XIII) as base oil were blended so that the blending rate of the organic phosphonate in the base oil might be as shown in Table 6, and dissolved uniformly to prepare lubricating oil compositions for refrigerating machine of Examples 41 to 49.

The same tests were conducted on the lubricating oil compositions for refrigerating machine of these Examples. The results are shown in Table 6 together with the result of Comparative Example 1.

Table 6

	blending rate of organic phosphonate (wt.%)	anti-wear property (wear ratio)	solubility (−50°C)			stability		
			3%	10%	50%	Fe	Cu	Al
Comparative Example 1	0	2.3	−	−	−	○	○	○
Example 41	0.01	0.2	○	○	○	○	○	○
Example 42	0.1	0	○	○	○	○	○	○
Example 43	1.0	0	○	○	○	○	○	○
Example 44	2.0	0	○	○	○	○	○	○
Example 45	10.0	0	○	○	○	○	○	○
Example 46	20.0	0	○	○	○	○	○	○
Example 47	50.0	0	○	○	○	○	○	○
Example 48	80.0	0	○	○	○	○	○	○
Example 49	100.0	0	○	○	○	○	○	○

It is known from Table 6 that the lubricating oil compositions for refrigerating machine of Examples 41 to 49 were excellent in solubility and stability, and was superior in anti-wear property to Comparative Example 1 which did not contain organic phosphonate.

Examples 50 to 57

In the same manner as in Examples 41 to 49 except that pentaerythritol tetraoctanoate was used as the base oil, the lubricating oil compositions for refrigerating machine of Examples 50 to 57 were prepared.

The same tests were conducted on these lubricating oil compositions for refrigerating machine of the Examples. The results are shown in Table 7 together with the results of Example 49 and Comparative Example 2.

Table 7

	blending rate of organic phosphonate (wt.%)	anti-wear property (wear ratio)	solubility (−50℃)			stability		
			3%	10%	50%	Fe	Cu	Al
Comparative Example 2	0	1.5	−	−	−	△	○	○
Example 50	0.01	0.1	○	○	○	○	○	○
Example 51	0.1	0	○	○	○	○	○	○
Example 52	1.0	0	○	○	○	○	○	○
Example 53	2.0	0	○	○	○	○	○	○
Example 54	10.0	0	○	○	○	○	○	○
Example 55	20.0	0	○	○	○	○	○	○
Example 56	50.0	0	○	○	○	○	○	○
Example 57	80.0	0	○	○	○	○	○	○
Example 49	100.0	0	○	○	○	○	○	○

It is known from Table 7 that the lubricating oil compositions for refrigerating machine of Examples 50 to 57 were excellent in solubility, and were superior in anti-wear property and stability to Comparative Example 2 which did not contain organic phosphonate.

Examples 58 to 65

In the same manner as in Examples 41 to 49 except that the fluorinated oil expressed in Formula (XIX) was used as the base oil, the lubricating oil compositions for refrigerating machine of Examples 58 to 65 were obtained.

The same tests were conducted on these compositions The results are shown in Table 8, together with the results of Example 49 and Comparative Example 3.

Table 8

	blending rate of organic phosphonate (wt.%)	anti-wear property (wear ratio)	solubility (−50°C)			stability		
			3%	10%	50%	Fe	Cu	Al
Comparative Example 3	0	2.0	-	-	-	○	○	○
Example 58	0.01	0.3	○	○	○	○	○	○
Example 59	0.1	0	○	○	○	○	○	○
·Example 60	1.0	0	○	○	○	○	○	○
Example 61	2.0	0	○	○	○	○	○	○
Example 62	10.0	0	○	○	○	○	○	○
Example 63	20.0	0	○	○	○	○	○	○
Example 64	50.0	0	○	○	○	○	○	○
Example 65	80.0	0	○	○	○	○	○	○
Example 49	100.0	0	○	○	○	○	○	○

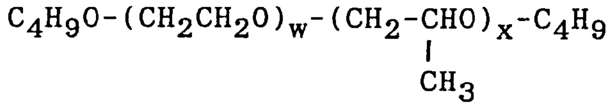
It is known from Table 8 that the compositions of Examples 58 to 65 were excellent in solubility and stability, and were superior in anti-wear property to Comparative Example 3 which did not contain organic phosphonate.

Examples 66 to 76

The organic phosphonate of which R^1 to R^3 in Formula (I) are commonly 2-ethylhexyl groups, was blended with the base oil shown in Table 9, and dissolved uniformly to prepare lubricating oil compositions for refrigerating machine of Examples 66 to 76. The blending rate of organic phosphonate in the base oil was 1.0 wt.%. In the base oil column of the table, the symbols represent the following compounds respectively.

P1: Polyalkylene glycol expressed in Formula (XIII)

P2: Polyalkylene glycol expressed in Formula (XXI), of which kinematic viscosity at 40 deg. C is 32 cSt.

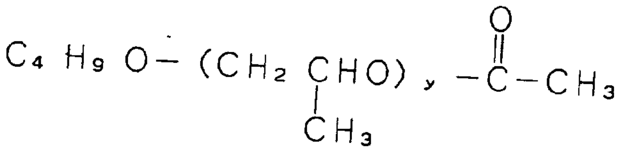


$$C_4H_9O-(CH_2CH_2O)_w-(CH_2-\underset{\substack{|\\CH_3}}{C}HO)_x-C_4H_9$$

(XXI)

where w and x are integers of which ratio w/x is 0.6.

P3: Polyalkylene glycol expressed in Formula (XXII), of which kinematic viscosity at 40 deg. C is 56 cSt.



$$C_4H_9O-(CH_2\underset{\substack{|\\CH_3}}{C}HO)_y-\overset{\substack{O\\\|}}{C}-CH_3$$

(XXII)

E1: Pentaerythritol tetraoctanoate

E2: Trimethylolpropane triheptanoate

E3: 1,14-Tetradecanoic acid dioctyl ester

E4: 1,16-Hexadecanoic acid dioctyl ester

E5: 1,9-Azelaic acid dioctyl ester

E6: Carbonate expressed in Formula (XVIa), of which kinematic viscosity at 40 deg. C is 32 cSt.

P1/E1 (99/1): Mixed base oil of 99 parts by weight of polyalkylene glycol of P1 and 1 part by weight of pentaerythritol tetraoctanoate of E1

P1/E1 (1/99): Mixed base oil of 1 part by weight of polyalkylene glycol of P1 and 99 parts by weight of pentaerythritol tetraoctanoate of E1

The same test were conducted on the lubricating oil compositions for refrigerating machine of these Examples The results are shown in Table 9.

Table 9

Example No.	base oil	anti-wear property (wear ratio)	solubility (−50℃)			stability		
			3%	10%	50%	Fe	Cu	Al
66	P^1	0	○	○	○	○	○	○
67	P^2	0	○	○	○	○	○	○
68	P^3	0	○	○	○	○	○	○
69	E^1	0	○	○	○	○	○	○
70	E^2	0	○	○	○	○	○	○
71	E^3	0	○	○	○	○	○	○
72	E^4	0	○	○	○	○	○	○
73	E^5	0	○	○	○	○	○	○
74	E^6	0	○	○	○	○	○	○
75	P^1/E^1(99/1)	0	○	○	○	○	○	○
76	P^1/E^1(1/99)	0	○	○	○	○	○	○

It is known-from Table 9 that the compositions of Examples 66 to 76 were all excellent in anti-wear property, solubility and stability.

Examples 77 to 99

The organic phosphate of which R^1 to R^3 in Formula (V) are substitutes shown in Tables 10, 11, and the base oil shown in the same tables were blended so that the blending rate of the organic phosphate in the base oil might be as shown in the tables, and dissolved uniformly to prepare lubricating oil compositions for refrigerating machine of Examples 77 to 99.

In the base oil column in Tables 10, 11, the symbols E and F represent the same compounds as mentioned above, and I denotes an organic phosphonate of which R^1, R^2, R^3 in Formula (I) are commonly 2-ethylhexyl groups, and of the organic phosphate column, the symbol TD denotes a tridecyl group and A is an allyl group. The other symbols represent the same substituents as specified above.

The compositions were similarly tested, of which results are shown in Tables 10, 11.

Table 10

Example No.	base oil	organic phosphate				anti-wear property (wear ratio)	solubility (−50°C)			stability		
		substituents			blending rate (wt.%)							
		R^1	R^2	R^3			3%	10%	50%	Fe	Cu	Al
77	E	M	M	TD	1.0	0.4	○	○	○	○	○	○
78	E	nB	nB	TD	1.0	0.3	○	○	○	○	○	○
79	E	EH	EH	TD	1.0	0	○	○	○	○	○	○
80	E	EH	EH	DD	1.0	0	○	○	○	○	○	○
81	E	EH	EH	nO	1.0	0	○	○	○	○	○	○
82	E	EH	EH	EH	1.0	0	○	○	○	○	○	○
83	F	EH	EH	EH	1.0	0	○	○	○	○	○	○
84	E	EH	EH	iO	1.0	0	○	○	○	○	○	○
85	E	EH	EH	nB	1.0	0	○	○	○	○	○	○
86	E	EH	EH	A	0.5	0	○	○	○	○	○	○
87	E	iO	iO	EH	1.0	0	○	○	○	○	○	○

Table 11

Example No.	base oil	organic phosphate				anti-wear property (wear ratio)	solubility (−50℃)			stability		
		substituents			blending rate (wt.%)							
		R¹	R²	R³			3%	10%	50%	Fe	Cu	Al
88	E	iO	iO	iO	1.0	0	○	○	○	○	○	○
89	F	iO	iO	iO	1.0	0	○	○	○	○	○	○
90	E	iO	iO	nH	1.0	0	○	○	○	○	○	○
91	E	EH	nO	nO	1.0	0	○	○	○	○	○	○
92	E	iO	iO	nO	1.0	0	○	○	○	○	○	○
93	E	nO	nO	nO	1.0	0	○	○	○	○	○	○
94	E	nO	nO	iO	1.0	0	○	○	○	○	○	○
95	E	D	D	DD	1.0	0	○	○	○	○	○	○
96	E	D	D	D	1.0	0	○	○	○	○	○	○
97	E	DD	DD	nB	1.0	0	○	○	○	○	○	○
98	E	DD	DD	DD	0.5	0	○	○	○	○	○	○
99	I	EH	EH	EH	1.0	0	○	○	○	○	○	○

It is known from these tables that the compositions of Examples 77 to 99 were excellent in all of anti-wear property, solubility, and stability.

Examples 100 to 102, Comparative Examples 10, 11

Same as used in the foregoing Examples and Comparative Examples, the polyalkylene glycol expressed in Formula (XIII) was used as the base oil at the moisture content of 1.0% without dehumidifying to 0.3% of moisture content as used in the foregoing Examples and Comparative Examples, and this base oil was blended with the organic phosphate of which R^1 to R^3 in Formula (V) are commonly 2-ethylhexyl groups at the blending rate of the organic phosphate in the base oil as shown in Table 12, and dissolved uniformly to prepare the lubricating oil compositions for refrigerating machine of Examples 100 to 102, and Comparative Example 11. Without adding organic phosphate, Comparative Example 10 was prepared.

The lubricating oil compositions for refrigerating machine of the Examples and Comparative Examples were tested, of which results are shown in Table 12, together with the results of Comparative Example 1.

Table 12

	blending rate of organic phosphate (wt.%)	moisture content (%)	anti-wear property (wear ratio)	stability		
				Fe	Cu	Al
Comparative Example 10	0	1.0	5.0	△	△	○
Comparative Example 11	8.0	1.0	0.5	△	○	○
Example 100	15.0	0.7	0.1	○	○	○
Example 101	50.0	0.5	0.0	○	○	○
Example 102	100.0	0.05	0.0	○	○	○
Comparative Example 1	0	0.3	2.3	○	○	○

It is known from Table 12 that, even in the same polyalkylene glycol, if the moisture content was high, the stability and anti-wear property were inferior when the organic phosphate was not added (Comparative Example 10) or the blending rate of organic phosphate was 10 wt.% or less (Comparative Example 11), but that when the organic phosphate was blended by more than 10.0 wt.% in Examples 100, 101, the stability and anti-wear property were excellent, even if the moisture content of polyalkylene glycol was high, same as in Example 102 fully composed of organic phosphate.

Examples 103 to 111

In the same manner as in Examples 100 to 102 except that pentaerythritol tetraoctanoate was used as the base oil, lubricating oil compositions for refrigerating machine of Examples 103 to 111 were prepared.

The compositions were tested, of which results are shown in Table 13 together with the results of Example 102 and Comparative Example 2.

Table 13

	blending rate of organic phosphate (wt.%)	anti-wear property (wear ratio)	solubility (-50°C)			stability		
			3%	10%	50%	Fe	Cu	Al
Comparative Example 2	0	1.5	-	-	-	△	○	○
Example 103	0.01	0.1	○	○	○	○	○	○
Example 104	0.1	0.1	○	○	○	○	○	○
Example 105	0.5	0.1	○	○	○	○	○	○
Example 106	1.0	0	○	○	○	○	○	○
Example 107	2.0	0	○	○	○	○	○	○
Example 108	10.0	0	○	○	○	○	○	○
Example 109	20.0	0	○	○	○	○	○	○
Example 110	50.0	0	○	○	○	○	○	○
Example 111	80.0	0	○	○	○	○	○	○
Example 102	100.0	0	○	○	○	○	○	○

It is known from Table 13 that the compositions of Examples 103 to 111 were all excellent in solubility, and superior to anti-wear property and stability to Comparative Example 2 which did not contain organic phosphate.

Examples 112 to 120

In the same manner as in Examples 100 to 102, except that the fluorinated oil expressed in Formula (XIX) was used as the base oil, the lubricating oil compositions for refrigerating machine of Examples 112 to 120 were prepared.

The compositions were tested, of which results are shown in Table 14 together with the results of Example 102 and Comparative Example 3.

Table 14

	blending rate of organic phosphate (wt.%)	anti-wear property (wear ratio)	solubility (-50°C)			stability		
			3%	10%	50%	Fe	Cu	Al
Comparative Example 3	0	2.0	–	–	–	○	○	○
Example 112	0.01	0.3	○	○	○	○	○	○
Example 113	0.1	0.1	○	○	○	○	○	○
Example 114	0.5	0.1	○	○	○	○	○	○
Example 115	1.0	0	○	○	○	○	○	○
Example 116	2.0	0	○	○	○	○	○	○
Example 117	10.0	0	○	○	○	○	○	○
Example 118	20.0	0	○	○	○	○	○	○
Example 119	50.0	0	○	○	○	○	○	○
Example 120	80.0	0	○	○	○	○	○	○
Example 102	100.0	0	○	○	○	○	○	○

It is known-from Table 14, the compositions of Examples 112 to 120 were excellent in solubility and stability, and superior in anti-wear property to Comparative Example 3 which did not contain organic phosphate.

Examples 121 to 128

The organic phosphate of which R^1 to R^3 in Formula (V) are commonly 2-ethylhexyl groups was blended with the base oil shown in Table 15, and dissolved uniformly to prepare the lubricating oil compositions for refrigerating machine of Examples 121 to 128. The blending rate of the organic phosphate in the base oil was 1.0 wt.%. The symbols in the base oil column in the table represent the same compounds as specified above. These compositions of the Examples were tested, of which results are shown in Table 15.

Table 15

Example No.	base oil	anti-wear property (wear ratio)	solubility (−50 °C)			stability		
			3 %	10 %	50 %	Fe	Cu	Al
121	E^1	0	○	○	○	○	○	○
122	E^2	0	○	○	○	○	○	○
123	E^3	0	○	○	○	○	○	○
124	E^4	0	○	○	○	○	○	○
125	E^5	0	○	○	○	○	○	○
126	E^6	0	○	○	○	○	○	○
127	P^1/E^1(99/1)	0	○	○	○	○	○	○
128	P^1/E^1(1/99)	0	○	○	○	○	○	○

It is known from Table 15 that the compositions of Examples 121 to 128 were excellent in the anti-wear property, solubility, and stability.

Examples 129 to 137

In the same manner as in Examples 121 to 128, except that the blending rate of the organic phosphate in the base oil was 10 wt.%, the lubricating oil compositions for refrigerating machine of Examples 129 to 137 were prepared.

The compositions of these Examples were tested, of which results are shown in Table 16.

Table 16

Example No.	base oil	anti-wear property (wear ratio)	solubility (−50°C)			stability		
			3%	10%	50%	Fe	Cu	Al
129	E^1	0	○	○	○	○	○	○
130	E^2	0	○	○	○	○	○	○
131	E^3	0	○	○	○	○	○	○
132	E^4	0	○	○	○	○	○	○
133	E^5	0	○	○	○	○	○	○
134	I	0	○	○	○	○	○	○
135	E^6	0	○	○	○	○	○	○
136	P'/E'(99/1)	0	○	○	○	○	○	○
137	P'/E'(1/99)	0	○	○	○	○	○	○

It is known-from Table 16 that the compositions of Examples 129 to 137 were excellent in anti-wear property, solubility and stability.

Examples 138 to 140

In the same manner as in Examples 121 to 128 except that the blending rate of organic phosphate in the base oil was 15 wt.% and that polyalkylene glycol expressed by symbols P^1, P^2, P^3 was used as the base oil, the lubricating oil compositions for refrigerating machine of Examples 138 to 140 were prepared.

The compositions of these Examples were tested, of which results are shown in Table 17.

Table 17

Example No.	base oil	anti-wear property (wear ratio)	solubility (−50°C)			stability		
			3%	10%	50%	Fe	Cu	Al
138	P^1	0	○	○	○	○	○	○
139	P^2	0	○	○	○	○	○	○
140	P^3	0	○	○	○	○	○	○

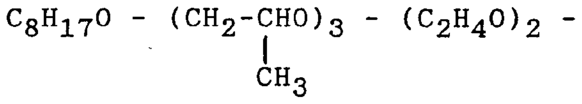
It is known from Table 17 that the compositions of Examples 138 to 140 were excellent in anti-wear property, solubility, and stability.

Examples 141 to 183

The organic phosphate of which groups in Formula (VI)
$[R^{11}O\text{-}\{(PO)_d - (EO)_e\}]$-(hereinafter called the first substituent)
$[R^{12}O\text{-}\{(PO)_f - (EO)_g\}]$-(hereinafter called the second substituent)
$[R^{13}O\text{-}\{(PO)_h - (EO)_i\}]$-
(hereinafter called the third substituent)
are substituents shown in Tables 18 to 21 was blended with the base oil shown in the same tables, and dissolved uniformly to prepare the lubricating oil compositions for refrigerating machine of Examples 141 to 183. The blending rate of the organic phosphate in the base oil was 1.0 wt.%.

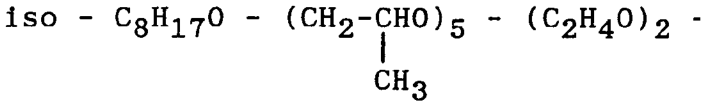
In the base oil column of Tables 18 to 21, the symbols P, E, F, V, I represent the same compounds as specified above, respectively, and the symbols in the organic phosphate column represent the following substituents, respectively.

(6) $C_{13}H_{27}O - (C_2H_4O)_2 -$
(7) $C_{10}H_{21}O - (C_2H_4O)_2 -$
(8) $C_8H_{17}O - (C_2H_4O)_2 -$ [where C_8H_{17}-is 2-ethylhexyl group]
(9) $C_8H_{17}O - (C_2H_4O)_5 -$ [where C_8H_{17}-is 2-ethylhexyl group]
(10) $C_8H_{17}O - (C_2H_4O)_{10}-$ [where C_8H_{17}-is 2-ethylhexyl group]
(11) $C_8H_{17}O - (C_2H_4O)_{30} -$ [where C_8H_{17}-is 2-ethylhexyl group]
(12) iso - $C_8H_{17}O - (C_2H_4O)_2 -$
(13) iso - $C_8H_{17}O - (C_2H_4O)_5 -$
(14) iso - $C_8H_{17}O - (C_2H_4O)_{10} -$
(15) n - $C_8H_{17}O - (C_2H_4O)_2 -$
(16) n - $C_4H_9O - (C_2H_4O)_2 -$
(17) n - $C_4H_9O - (C_2H_4O)_5 -$
(18)



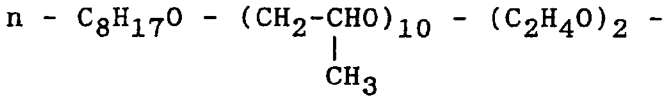
$$C_8H_{17}O - (CH_2\text{-}\underset{\displaystyle CH_3}{\underset{|}{C}}HO)_3 - (C_2H_4O)_2 -$$

[where C_8H_{17}-is 2-ethylhexyl group]
(19)



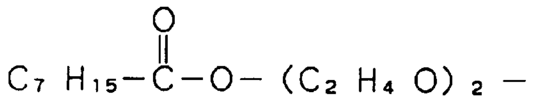
$$\text{iso} - C_8H_{17}O - (CH_2\text{-}\underset{\displaystyle CH_3}{\underset{|}{C}}HO)_5 - (C_2H_4O)_2 -$$

(20)



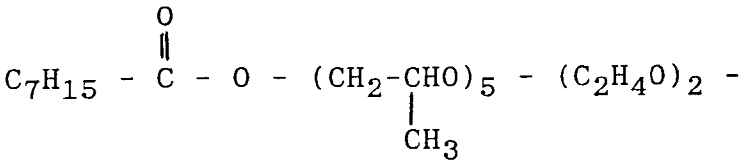
$$\text{n} - C_8H_{17}O - (CH_2\text{-}\underset{\displaystyle CH_3}{\underset{|}{C}}HO)_{10} - (C_2H_4O)_2 -$$

(21) $C_{10}H_{21}O - (C_2H_4O)_5 -$
(22) $C_{10}H_{21}O - (C_2H_4O)_{15} -$
(23)



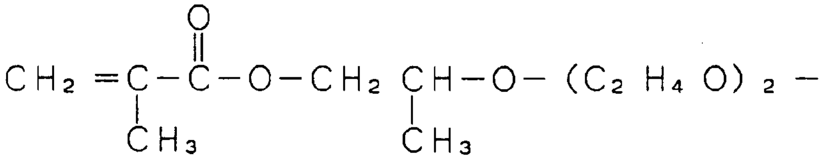
$$C_7H_{15}-\overset{\displaystyle O}{\overset{\|}{C}}-O-(C_2H_4O)_2-$$

(24)



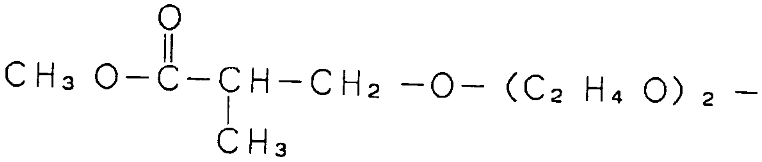
$$C_7H_{15}-\overset{\overset{O}{\|}}{C}-O-(CH_2-\underset{\underset{CH_3}{|}}{C}HO)_5-(C_2H_4O)_2-$$

(25)



$$CH_2=\underset{\underset{CH_3}{|}}{C}-\overset{\overset{O}{\|}}{C}-O-CH_2\underset{\underset{CH_3}{|}}{C}H-O-(C_2H_4O)_2-$$

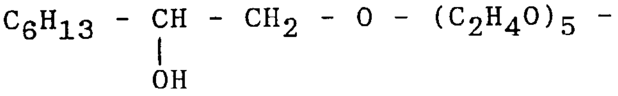
(26)



$$CH_3O-\overset{\overset{O}{\|}}{C}-\underset{\underset{CH_3}{|}}{C}H-CH_2-O-(C_2H_4O)_2-$$

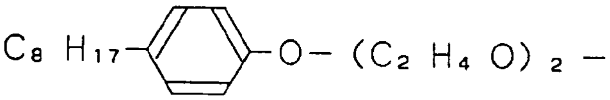
(27) polyoxyethylene of lanolin alcohol

(28)

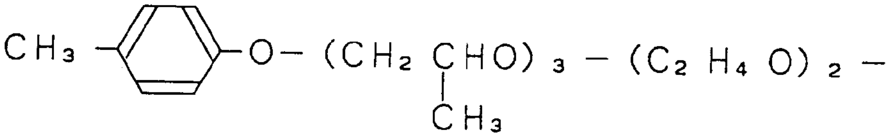


$$C_6H_{13}-\underset{\underset{OH}{|}}{CH}-CH_2-O-(C_2H_4O)_5-$$

(29)



(30)



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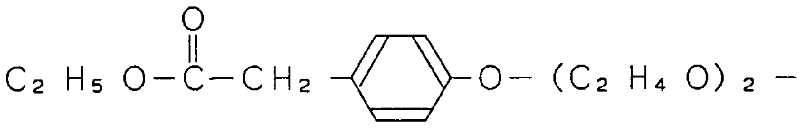

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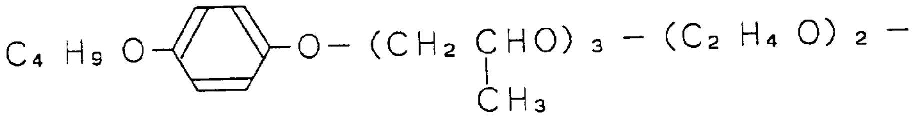
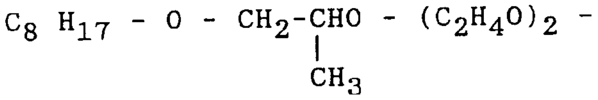
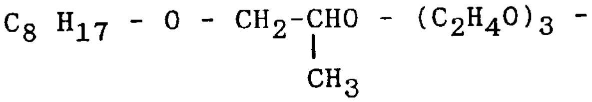


(33) C_8H_{17} - O - [where C_8H_{17}-is 2-ethylhexyl group]
(34) $C_{13}H_{27}O$ - $(C_2H_4O)_5$ -
(35) sec - C_{11-15} - O - $(C_2H_4O)_5$ - [where sec-C_{11-15}- is a mixture of secondary alkyl group with 11 to 15 carbon atoms]
(36) C_{6-10} - O - $(CH_2\text{-}CHO)_3$ - $(C_2H_4O)_2$ - CH_3 [where C_{6-10}- is a mixture of alkyl group with 6 to 10 carbon atoms]
(37)



$C_8H_{17}-O-CH_2-\underset{CH_3}{\underset{|}{CHO}}-(C_2H_4O)_2-$

[where C_8H_{17}-is 2-ethylhexyl group]
(38)



$C_8H_{17}-O-CH_2-\underset{CH_3}{\underset{|}{CHO}}-(C_2H_4O)_3-$

[where C_8H_{17}-is 2-ethylhexyl group]
The compounds were tested, of which results are shown in Tables 18 to 21.

Table 18

Example No.	base oil	organic phosphate			anti-wear property (wear ratio)	solubility (−50°C)			stability		
		first substituent	second substituent	third substituent		3 %	10 %	50 %	Fe	Cu	Al
141	E	(6)	(6)	(6)	0. 3	○	○	○	○	○	○
142	E	(7)	(7)	(7)	0. 2	○	○	○	○	○	○
143	P	(8)	(8)	(8)	0	○	○	○	○	○	○
144	E	(8)	(8)	(8)	0	○	○	○	○	○	○
145	F	(8)	(8)	(8)	0	○	○	○	○	○	○
146	E	(9)	(9)	(9)	0	○	○	○	○	○	○
147	E	(10)	(10)	(10)	0	○	○	○	○	○	○
148	E	(11)	(11)	(11)	0	○	○	○	○	○	○
149	P	(12)	(12)	(12)	0	○	○	○	○	○	○
150	E	(13)	(13)	(13)	0	○	○	○	○	○	○

Table 19

Example No.	base oil	organic phosphate			anti-wear property (wear ratio)	solubility (−50℃)			stability		
		first substituent	second substituent	third substituent		3 %	10 %	50 %	Fe	Cu	Al
151	E	(14)	(14)	(14)	0	○	○	○	○	○	○
152	E	(15)	(15)	(15)	0	○	○	○	○	○	○
153	P	(16)	(16)	(16)	0.1	○	○	○	○	○	○
154	E	(16)	(16)	(16)	0.1	○	○	○	○	○	○
155	E	(17)	(17)	(17)	0.1	○	○	○	○	○	○
156	E	(8)	(8)	(12)	0	○	○	○	○	○	○
157	E	(8)	(15)	(15)	0	○	○	○	○	○	○
158	E	(8)	(8)	(7)	0	○	○	○	○	○	○
159	P	(18)	(18)	(18)	0	○	○	○	○	○	○
160	E	(18)	(18)	(18)	0	○	○	○	○	○	○

Table 20

Example No.	base oil	organic phosphate			anti-wear property (wear ratio)	solubility (−50°C)			stability		
		first substituent	second substituent	third substituent		3 %	10 %	50 %	Fe	Cu	Al
161	F	(18)	(18)	(18)	0	○	○	○	○	○	○
162	E	(19)	(19)	(19)	0	○	○	○	○	○	○
163	E	(20)	(20)	(20)	0	○	○	○	○	○	○
164	E	(21)	(21)	(21)	0	○	○	○	○	○	○
165	E	(22)	(22)	(22)	0	○	○	○	○	○	○
166	E	(23)	(23)	(23)	0	○	○	○	○	○	○
167	E	(24)	(24)	(24)	0	○	○	○	○	○	○
168	E	(25)	(25)	(25)	0	○	○	○	○	○	○
169	E	(26)	(26)	(26)	0	○	○	○	○	○	○
170	E	(27)	(27)	(27)	0	○	○	○	○	○	○

Table 21

Example No.	base oil	organic phosphate			anti-wear property (wear ratio)	solubility (−50℃)			stability		
		first substituent	second substituent	third substituent		3%	10%	50%	Fe	Cu	Al
171	E	(28)	(28)	(28)	0	○	○	○	○	○	○
172	E	(29)	(29)	(29)	0	○	○	○	○	○	○
173	E	(30)	(30)	(30)	0	○	○	○	○	○	○
174	E	(31)	(31)	(31)	0	○	○	○	○	○	○
175	E	(32)	(32)	(32)	0	○	○	○	○	○	○
176	E	(33)	(9)	(9)	0	○	○	○	○	○	○
177	E	(33)	(33)	(34)	0	○	○	○	○	○	○
178	E	(33)	(33)	(35)	0	○	○	○	○	○	○
179	E	(33)	(33)	(36)	0	○	○	○	○	○	○
180	E	(37)	(37)	(37)	0	○	○	○	○	○	○
181	E	(38)	(38)	(38)	0	○	○	○	○	○	○
182	V	(8)	(8)	(8)	0	○	○	○	○	○	○
183	I	(8)	(8)	(8)	0	○	○	○	○	○	○

It is known from these tables that the compositions of Examples 141 to 183 were excellent in anti-wear property, solubility and stability.

Examples 184 to 193

The organic phosphate of which the first to the third substituents in Formula (VI) are commonly the group of symbol (8) above, and the polyalkylene glycol expressed in Formula (XIII) as base oil were blended so that the blending rate of the organic phosphate in the base oil might be as shown in Table 22, and dissolved uniformly, and the lubricating oil compositions for refrigerating machine of Examples 184 to 193 were prepared.

The compositions of these Examples were tested, of which results are shown in Table 22, together with the result of Comparative Example 1.

Table 22

	blending rate of organic phosphate (wt.%)	anti-wear property (wear ratio)	solubility (−50°C)			stability		
			3%	10%	50%	Fe	Cu	Al
Comparative Example 1	0	2.3	–	–	–	○	○	○
Example 184	0.01	0.2	○	○	○	○	○	○
Example 185	0.1	0	○	○	○	○	○	○
Example 186	0.5	0	○	○	○	○	○	○
Example 187	1.0	0	○	○	○	○	○	○
Example 188	2.0	0	○	○	○	○	○	○
Example 189	10.0	0	○	○	○	○	○	○
Example 190	20.0	0	○	○	○	○	○	○
Example 191	50.0	0	○	○	○	○	○	○
Example 192	80.0	0	○	○	○	○	○	○
Example 193	100.0	0	○	○	○	○	○	○

It is known from Table 22 that the compositions of Examples 184 to 193 were excellent in solubility and stability, and superior in anti-wear property to Comparative Example 1 which did not contain organic phosphate.

Examples 194 to 202

In the same manner as in Examples 184 to 193 except that pentaerythritol tetraoctanoate was used as the base oil, the lubricating oil compositions for refrigerating machine of Examples 194 to 202 were prepared.

The compositions of these Examples were tested, of which results are shown in Table 23 together with the results of Example 193 and Comparative Example 2.

Table 23

	blending rate of organic phosphate (wt.%)	anti-wear property (wear ratio)	solubility (−50℃)			stability		
			3%	10%	50%	Fe	Cu	Al
Comparative Example 2	0	1.5	-	-	-	△	○	○
Example 194	0.01	0.1	○	○	○	○	○	○
Example 195	0.1	0	○	○	○	○	○	○
Example 196	0.5	0	○	○	○	○	○	○
Example 197	1.0	0	○	○	○	○	○	○
Example 198	2.0	0	○	○	○	○	○	○
Example 199	10.0	0	○	○	○	○	○	○
Example 200	20.0	0	○	○	○	○	○	○
Example 201	50.0	0	○	○	○	○	○	○
Example 202	80.0	0	○	○	○	○	○	○
Example 193	100.0	0	○	○	○	○	○	○

It is known from Table 23 that the compositions of Examples 194 to 202 were excellent in solubility, and superior in anti-wear property and stability to Comparative Example 2 which did not contain organic phosphate.

Examples 203 to 211

In the same manner as in Examples 184 to 193 except that the fluorinated oil expressed in Formula (XIX) was used as the base oil, the lubricating oil compositions for refrigerating machine of Examples 203 to 211 were prepared.

The compositions of the Examples were tested, of which results are shown in Table 24 together with the results of Example 193 and Comparative Example 3.

Table 24

	blending rate of organic phosphate (wt.%)	anti-wear property (wear ratio)	solubility (−50°C)			stability		
			3%	10%	50%	Fe	Cu	Al
Comparative Example 3	0	2.0	−	−	−	○	○	○
Example 203	0.01	0.3	○	○	○	○	○	○
Example 204	0.1	0	○	○	○	○	○	○
Example 205	0.5	0	○	○	○	○	○	○
Example 206	1.0	0	○	○	○	○	○	○
Example 207	2.0	0	○	○	○	○	○	○
Example 208	10.0	0	○	○	○	○	○	○
Example 209	20.0	0	○	○	○	○	○	○
Example 210	50.0	0	○	○	○	○	○	○
Example 211	80.0	0	○	○	○	○	○	○
Example 193	100.0	0	○	○	○	○	○	○

It is known from Table 24 that the compositions of Examples 203 to 211 were excellent in solubility and stability, and superior in anti-wear property to Comparative Example 3 which did not contain organic phosphate.

Examples 212 to 222

The organic phosphate of which the first to the third substituents in Formula (VI) are commonly the group of symbol (8) above was blended with the base oil in Table 25, and dissolved uniformly to prepare the lubricating oil compositions for refrigerating machine of Examples 212 to 222. The blending rate of organic phosphate in the base oil was 1.0 wt.%. The symbols in the base oil column in the table denote the same compounds as specified above.

The compositions of these Examples were tested, of which results are shown in Table 25.

Table 25

Example No.	base oil	anti-wear property (wear ratio)	solubility (−50°C) 3%	10%	50%	stability Fe	Cu	Al
212	P^1	0	○	○	○	○	○	○
213	P^2	0	○	○	○	○	○	○
214	P^3	0	○	○	○	○	○	○
215	E^1	0	○	○	○	○	○	○
216	E^2	0	○	○	○	○	○	○
217	E^3	0	○	○	○	○	○	○
218	E^4	0	○	○	○	○	○	○
219	E^5	0	○	○	○	○	○	○
220	E^6	0	○	○	○	○	○	○
221	P^1/E^1(99/1)	0	○	○	○	○	○	○
222	P^1/E^1(1/99)	0	○	○	○	○	○	○

It is known from Table 25 that the compositions in Examples 212 to 222 were excellent in anti-wear property, solubility, and stability.

Examples 223 to 230, Comparative Examples 12 to 14

The organic phosphorus compounds and base oil shown in Table 26 were blended so that the blending rate of the organic phosphorus compound in the base oil might be 10 wt.%, and dissolved uniformly, and the sample compositions of which total acid value is 0.00[mg KOH/g] were prepared.

When the sample composition comprised ester base fluid as base oil, the fatty acid which is material of the ester base fluid was added to the sample composition, and when the sample composition comprised polyalkylene glycol as base oil, the decomposition product of the polyalkylene glycol was added to the sample composition. Therefore the lubricating oil compositions for refrigerating machine of Examples 223 to 230 and Comparative Examples 12 to 14 adjusted the total acid value as shown in the table were prepared.

The symbols in the organic phosphorus compound column and base oil column in the table represent the same compounds as defined above.

The compositions of these Examples and Comparative Examples were tested, of which results are shown in Table 26

Table 26

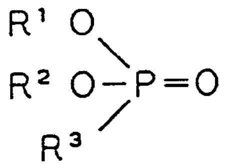
	organic phosphorous compound	base oil	total acid value	anti-wear property (wear ratio)	solubility (−50°C)			stability		
					3%	10%	50%	Fe	Cu	Al
Example 223	I	P'	0.00	0.0	○	○	○	○	○	○
Example 224	I	E'	0.00	0.0	○	○	○	○	○	○
Example 225	I	V	0.00	0.0	○	○	○	○	○	○
Example 226	I	E'	0.01	0.0	○	○	○	○	○	○
Example 227	V	P'	0.00	0.0	○	○	○	○	○	○
Example 228	V	E'	0.00	0.0	○	○	○	○	○	○
Example 229	V	F	0.00	0.0	○	○	○	○	○	○
Example 230	V	I	0.00	0.0	○	○	○	○	○	○
Comparative Example 12	I	E'	0.03	1.0	○	○	○	△	○	○
Comparative Example 13	I	P'	0.05	1.2	○	○	○	△	○	○
Comparative Example 14	V	E'	0.10	5.0	○	○	○	×	×	○

It is known from Table 26 that the lubricating oil compositions for refrigerating machine of Examples 223 to 230 of which acid value is 0.01 or less were similar in the solubility, but superior in anti-wear property and stability to the Comparative Examples of which acid values were all over 0.01.

Claims

1. A lubricating oil composition

comprising at least one organic phosphorus compound selected from a group comprising organic phosphonate expressed in Formula (I), organic phosphate expressed in Formula (V), and organic phosphate expressed in Formula (VI), out of polyalkylene glycol, ester base fluid, fluorinated oil and organic phosphorus compound as specified above, wherein, if composed of polyalkylene glycol and the organic phosphate expressed in Formula (V), the content of the organic phosphate in the base oil exceeds 10 wt.%.



(I)

where R^1, R^2 are either identical or different, expressing any one of the groups (1) to (4) below.

(1) an alkyl group with 1 to 18 carbon atoms,

(2) an alkenyl group with 3 to 18 carbon atoms,

(3) an aryl group with 6 to 18 carbon atoms (however, an alkyl group with 1 to 12 carbon atoms, or an alkenyl group with 2 to 12 carbon atoms may be possessed as a substitutent), and

(4) a polyoxyalkylene alkylether group expressed in Formula (II)

$$R^4O - (R^5O)_a - R^5 - \qquad (II)$$

(where R^4 denotes a hydrogen atom, an alkyl group with 1 to 18 carbon atoms, or an alkenyl group with 3 to 18 carbon atoms, R^5 represents an alkylene group with 2 to 4 carbon atoms, and a is 0 or an integer of 1 or more), and

R^3 denotes any one of the groups of (5) to (11):

(5) an alkyl group with 1 to 18 carbon atoms,

(6) an alkenyl group with 2 to 18 carbon atoms,

(7) an aryl group with 6 to 18 carbon atoms (an alkyl group with 1 to 12 carbon atoms or an alkenyl group with 2 to 12 carbon atoms may be possessed as a substituent),

(8) an polyoxyalkylene alkylether group expressed in Formula (IIa)

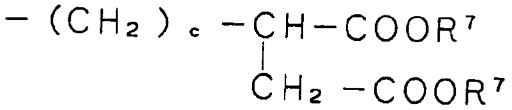
$$R^4O - (R^5O)_a - R^{21} - \qquad (IIa)$$

(where R^4, R^5 denote the same groups as above, R^{21} is an alkylene group with 1 to 4 carbon atoms, and a is the same integer as above),

(9) a group expressed in Formula (III)

(III) [where R^6 denotes any one of an alkyl group with 1 to 18 carbon atoms, an alkenyl group with 3 to 18 carbon atoms, an aryl group with 6 to 18 carbon atoms (an alkyl group with 1 to 12 carbon atoms or an alkenyl group with 2 to 12 carbon atoms may be possessed as a substituent), and a polyoxyalkylene alkylether group expressed in Formula (II), and b is an integer from 1 to 3],

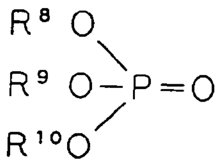
(10) a group expressed in Formula (IV)



$$-(CH_2)_c-\underset{\substack{|\\ CH_2-COOR^7}}{CH}-COOR^7 \qquad (IV)$$

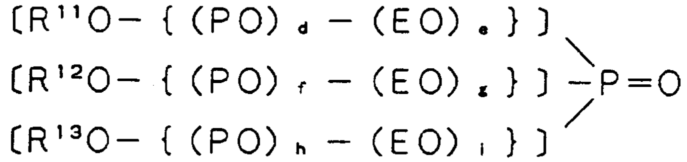
[where R^7 denotes any one of an alkyl group with 1 to 18 carbon atoms, an alkenyl group with 3 to 18 carbon atoms, an aryl group with 6 to 18 carbon atoms (an alkyl group with 1 to 12 carbon atoms or an alkenyl group with 2 to 12 carbon atoms may be possessed as a substituent), and a polyoxyalkylene alkylether group expressed in Formula (II), and c is 0 or 1], and

(11) a bezoyl group which may possess an alkyl group with 1 to 12 carbon atoms or an alkenyl group with 2 to 12 carbon atoms as a substituent



(V)

[where R^8, R^9, and R^{10} are either identical or different, expressing an alkyl group with 1 to 18 carbon atoms, or an alkenyl group with 3 to 18 carbon atoms],



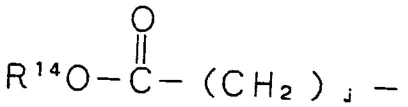
(VI)

[where R^{11}, R^{12}, and R^{13} are either identical or different, expressing any one of the groups (A) to (E) below, EO denotes an oxyethylene group, and PO represents an oxypropylene group; d to i denote 0 or integers of 1 or more, but d to i are not 0 at the same time; or when both d and e are integers of 1 or more, or when both f and g are integers of 1 or more, or when both h and i are integers of 1 or more, the oxyethylene group and oxypropylene group may be either bonded at random or bonded in block];

(A) an alkyl group with 1 to 18 carbon atoms,

(B) an alkenyl group with 3 to 18 carbon atoms,

(C) an aryl group with 6 to 18 carbon atoms (which may possess, however, either one of the groups, that is, an alkyl group with 1 to 12 carbon atoms, an alkenyl group with 2 to 12 carbon atoms, a group expressed in Formula (VII), or a group expressed in Formula (VIII), as a substituent),



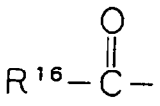
$$R^{14}O-\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_j- \qquad (VII)$$

(where R^{14} denotes an alkyl group with 1 to 18 carbon atoms, or an alkenyl group with 3 to 18 carbon atoms, and j is an integer from 2 to 15),

$R^{15}O-$ (VIII)

(where R^{15} denotes an alkyl group with 1 to 8 carbon atoms, or an alkenyl group with 3 to 8 carbon atoms),

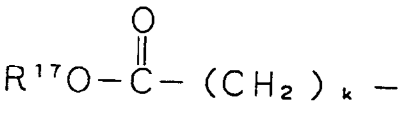
(D) a group expressed in Formula (IX),



$$R^{16}-\overset{\overset{\displaystyle O}{\|}}{C}- \qquad (IX)$$

[where R^{16} is an alkyl group with 1 to 18 carbon atoms, an alkenyl group with 2 to 18 carbon atoms, or an aryl group with 6 to 18 carbon atoms (which, however, may possess an alkyl group with 1 to 12 carbon atoms, or an alkenyl group with 2 to 12 carbon atoms as a substituent)], and

(E) a group expressed in Formula (X)



$$R^{17}O-\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_k- \qquad (X)$$

[where R^{17} is an alkyl group with 1 to 18 carbon atoms, an alkenyl group with 2 to 18 carbon atoms, or an aryl group with 6 to 18 carbon atoms (which, however, may possess either an alkyl group with 1 to 12 carbon atoms or an alkenyl group with 2 to 12 carbon atoms as a substituent), and k is an integer from 2 to 15].

2. A lubricating oil composition of claim 1, wherein the acid value is 0.01 or less.

3. Use of a lubricating oil composition according to claim 1 or 2, for a refrigerating machine.

European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 92 10 6937

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.5)
X	WO-A-9 009 387 (THE LUBRIZOL CORPORATION) * page 6, line 7 - page 7, line 28 * * page 15, line 7 - line 13 * ---	1,3	C10M105/74 C10M111/02 C10M111/04 C10M169/04 C10M171/00 C09K5/04 //(C10N40:30)
P,X	WO-A-9 118 073 (THE LUBRIZOL CORPORATION) * page 9, line 1 - page 11 * * page 16, line 7 - line 21 * ---	1,3	
X	EP-A-0 384 724 (NIPPON OIL LTD) * page 3, line 46 - line 57 * * page 6, line 1 - line 28 * ---	1,3	
P,X	EP-A-0 435 253 (NIPPON OIL LTD) * page 7, line 23 - line 28 * ---	1,3	
P,X	EP-A-0 461 262 (IDEMITSU KOSAN COMPANY LIMITED) * page 5, line 47 * ---	1,3	
X	DIE CHEM. TECHN. INDUSTRIE; SEIFEN,öLE,FETTE,WACHSE no. 23, 11 November 1971, AUGSBURG pages 881 - 886; DR. LEOPOLDINE RÖGLSPERGER: 'Phosphatester als Schmierbestandteile' * page 884, left column, line 53 - line 60; table 4 * * page 884, right column, line 63 - page 885, left column, line 3 * ---	1	**TECHNICAL FIELDS SEARCHED (Int. Cl.5)** C10M C09K
X	WORLD PATENTS INDEX LATEST Week 8320, Derwent Publications Ltd., London, GB; AN 83-48239K & JP-A-58 061 173 (MATSUSHITA ELEC IND KK) 12 April 1983 * abstract * ---	1,3	
X	US-A-4 857 215 (J.L WONG) * column 2, line 67 - column 3, line 9 *	1	

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	22 JULY 1992	HILGENGA K.J.

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