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REFRIGERATION LUBRICANTS

This invention relates to lubricants used with
 refrigerants, and more particularly to lubricants
 suitable for use in the compression of refrigerants
 containing no chlorine such as hydrofluorocarbons (HFC),
 05 preferably HFC-134a (1,1,1,2-tetrafluoroethane) and the
 like.

Heretofore, compounds containing fluorine and
 chlorine as a constituent element such as R-11
 (trichloromonofluoromethane), R-12 (dichlorodifluoro-
 10 methane) as a chlorofluorocarbon (CFC), R-22
 (monochlorodifluoromethane) as a hydrochlorofluorocarbon
 (HCFC) and the like have been used as a refrigerant for
 freezers, air conditioners, refrigerators and the like.
 In connection with recent problem on breakage of ozone
 15 layer, new refrigerants containing no chlorine such as
 HFC-134a and so on are proposed as a possible replace-
 ment for R-12, causing no breakage of ozone layer.

As a refrigeration lubricant, there are known
 many mineral-series and synthetic oils. However, it has
 20 been confirmed that these oils are very poor in the com-
 patibility with HFC-134a and can not be applied thereto.
 Therefore, it is important to take a countermeasure on
 this problem at the present. Furthermore, the lubricity,



electric insulating property, energy saving property, anti-wear performance, sealability, thermal stability, prevention of sludge formation and the like are mentioned as performances required in the refrigeration
05 lubricant, so that they are required to be considered in the development of the above countermeasure.

Incidentally, there have hitherto been known polyether series synthetic lubricants as a synthetic oil, which are reported in Journal of the Oil Chemistry,
10 vol. 29, No. 9, pp 336-343 (1980) and Journal of the Petroleum Technology, vol. 8, No. 6, pp 562-566 (1985). Furthermore, Japanese Patent laid open No. 61-281199 describes a mixture of polyglycol represented by a general formula of $R_1[O-(R_2O)_m-R_3]_n$, an alkylbenzene and
15 the like, and Japanese Patent laid open No. 57-63395 describes an oil obtained by mixing a polyether such as high molecular weight polyoxypropylene monobutyl ether with an epoxycycloalkyl compound, and Japanese Patent laid open No. 59-117590 describes a high viscosity mixed
20 oil of a polyether compound and a paraffinic or naphthanic mineral oil.

However, the conventional synthetic lubricants as mentioned above can not be a refrigeration lubricant using HFC-134a as a refrigerant from a viewpoint of
25 compatibility and the like.

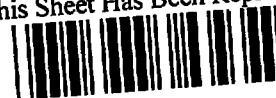
In US Patent No. 4,755,316, polyoxyalkylene



glycol (hereinafter abbreviated as PAG) having hydroxyl groups (-OH) at both terminals is reported as a refrigeration lubricant using HFC-134a. Further, it is described that PAG is dissolved in HFC-134a within a
05 wide temperature range as compared with general PAG containing hydroxyl group and alkyl group at its terminals, whereby the recycle of the lubricant into a compressor is improved in the refrigeration system and the seizing in the actuation of the compressor at high
10 temperature is prevented. Moreover, the temperature range compatible with HFC-134a is described to be between -40°C and +50°C.

On the contrary, HFC-134a is a replacing refrigerant of R-12 and is mainly expected for use in a
15 car air conditioner, a refrigerator and the like. In case of the refrigerator, it is required to have a good compatibility between lubricant and refrigerant, and further the lubricant itself is necessary to have an electric insulating property because the motor is
20 substantially existent in the refrigeration system. However, the conventional compounds examined as a lubricant for HFC-134a refrigerant inclusive of PAG disclosed in US Patent No. 4,755,316 are remarkably poor in the electric insulating property as compared with the
25 conventional refrigeration mineral oil and high in the hygroscopicity.

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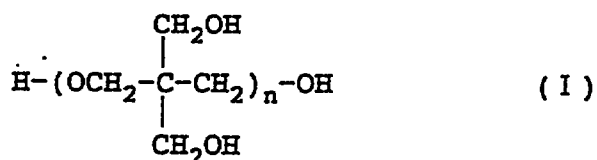
It is, therefore, an object of the invention to provide a refrigeration lubricant having an excellent compatibility with a new refrigerant such as HFC-134a or the like within a wide temperature range, a high
05 electric insulating property and a low hygroscopicity.

At the present, a part of commercially available esters is used in systems using refrigerants R-12, R-22 and the like, but is incompatible with HFC-134a as a new refrigerant or is very narrow in the compatible range
10 therewith. In this connection, the inventors have aimed at the fact that the ester has a high electric insulating property, a low hygroscopicity, a good lubricity and a high stability as compared with PAG and made various studies with respect to the molecule design of the ester
15 showing a wide range of compatibility with HFC-134a, and found that only esters having a considerably restricted structure can be used in the HFC-134a refrigeration system, and as a result, the invention has been accomplished.

20 According to a first aspect of the invention, there is the provision of a lubricant for hydrofluorocarbon refrigerant such as HFC-134a and the like comprising as a main component an ester comprised of neopentyl glycol and at least one straight or branched-
25 chain monovalent fatty acid having a carbon number of 3-18.

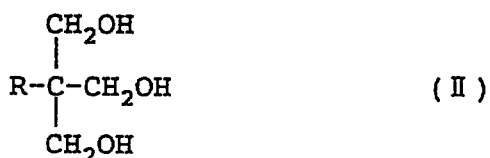


According to a second aspect of the invention, there is the provision of a lubricant for hydrofluoro-carbon refrigerant such as HFC-134a and the like comprising as a main component an ester comprised of at least one of pentaerythritol, dipentaerythritol and tripentaerythritol represented by the following general formula (I):



(in which n is 1, 2 or 3), and at least one straight or branched-chain monovalent fatty acid having a carbon number of 2-18.

According to a third aspect of the invention, there is the provision of a lubricant for hydrofluoro-carbon refrigerant such as HFC-134a and the like comprising as a main component an ester comprised of a polyvalent alcohol represented by the following general formula (II):



(in which R is an alkyl group having a carbon number of not more than 3), at least one straight or branched-chain monovalent fatty acid having a carbon number of



2-18, and not more than 25 mol% per total fatty acid of at least one polybasic acid having a carbon number of 4-36.

In a preferred embodiment of the invention, the
05 hydrofluorocarbon refrigerant is 1,1,1,2-tetrafluoroethane (HFC-134a).

The refrigeration lubricant for refrigerant HFC-134a and the like according to the first invention comprises an ester obtained by esterifying neopentyl
10 glycol with at least one straight or branched-chain monovalent fatty acid having a carbon number of 3-18 as a main component.

In the first invention, the reason why the carbon number of the monovalent fatty acid is limited to
15 3-18 is due to the fact that when the carbon number is less than 3, the viscosity is too low, while when it exceeds 18, the resulting ester becomes cloudy or becomes very poor in the compatibility with the refrigerant HFC-134a and the like.

20 As the monovalent fatty acid, mention may be made of propionic acid, isopropionic acid, butanoic acid, isobutanoic acid, pentanoic acid, isopentanoic acid, hexanoic acid, heptanoic acid, isoheptanoic acid, octanoic acid, 2-ethyl hexanoic acid, nonanoic acid,
25 3,5,5-trimethyl hexanoic acid, decanoic acid, undecanoic acid, lauric acid, myristic acid, palmitic acid,



palmitooleic acid, stearic acid, isostearic acid, oleic acid, and the like.

In the first invention, at least one of these monovalent fatty acids is properly mixed and esterified
05 with neopentyl glycol to obtain an ester satisfying desirable physical properties required for various refrigerators.

In order to obtain a sufficiently satisfactory compatibility with the refrigerant HFC-134a and the
10 like, it is preferable to use a mixture of straight chain fatty acid having a carbon number of 3-11, preferably 5-10 and a branched-chain fatty acid having a carbon number of 3-14, preferably 7-9 as the monovalent fatty acid. In this case, the amount of the straight or
15 branched-chain fatty acid used is preferable to be not less than 50 mol% per the total monovalent fatty acid used.

According to the invention, in order to give a proper viscosity to the resulting ester, at least one
20 polybasic acid having a carbon number of 4-36 may be esterified with neopentyl glycol in an amount of not more than 80 mol% per total fatty acid. Among the polybasic acids, considering the more compatibility with the refrigerant HFC-134a and the like and the physical
25 properties of the resulting ester, a polybasic acid having a carbon number of 4-10 is preferable.



Concretely, the polybasic acid includes succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, phthalic acid, maleic acid, trimellitic acid and so on. Moreover, the polybasic
05 acid having a carbon number of not more than 3 is a special product and is difficult to be cheaply available and is poor in the stability of the ester after the synthesis. While, when the carbon number exceeds 36, the compatibility of the resulting ester with HFC-134a
10 and the like is largely lowered. In the invention, the reason why the amount of the polybasic acid added is limited to not more than 80 mol% per the total fatty acid is due to the fact that when it exceeds 80 mol%, the gelation may be caused and it is difficult to obtain
15 desirable physical properties.

The ester compounds according to the first invention can be obtained by the esterification reaction through dehydration reaction between the specified polyvalent alcohol and the specified fatty acid as
20 mentioned above, or the general esterification reaction through an acid anhydride, an acid chloride or the like as a derivative of the fatty acid.

Since the ester according to the invention can be obtained by the above method, the remaining acid
25 value and hydroxyl value are not particularly critical. However, when the acid value exceeds 3, there may be

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caused an unfavorable phenomenon that the metal soap is formed and precipitated by the reaction with a metal used inside the refrigerator, so that the acid value is preferable to be not more than 3. Furthermore, when the
05 hydroxyl value exceeds 50, there may be caused an unfavorable phenomenon that the resulting ester becomes cloudy, so that the hydroxyl value is preferable to be not more than 50.

The lubricant for refrigerant HFC-134a and the
10 like according to the second invention comprises an ester obtained by esterifying at least one of pentaerythritol, dipentaerythritol and tripentaerythritol represented by the aforementioned general formula (I) with at least one straight or branched-chain
15 monovalent fatty acid having a carbon number of 2-18 as a main component.

In the condensate of pentaerythritol, the polymerization degree may be determined in accordance with the viscosity required in the resulting synthesized
20 ester.

In the second invention, the carbon number of the monovalent fatty acid is limited to 2-18 because when it exceeds 18, the resulting ester becomes cloudy or becomes very poor in the compatibility with the
25 refrigerant HFC-134a and the like.

As the monovalent fatty acid, mention may be

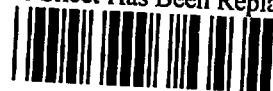


made of acetic acid, propionic acid, isopropionic acid,
butanoic acid, isobutanoic acid, pentanoic acid,
isopentanoic acid, hexanoic acid, heptanoic acid,
isoheptanoic acid, octanoic acid, 2-ethyl hexanoic acid,
05 nonanoic acid, 3,5,5-trimethyl hexanoic acid, decanoic
acid, undecanoic acid, lauric acid, myristic acid,
palmitic acid, palmitooleic acid, stearic acid,
isostearic acid, oleic acid, linoleic acid, linolenic
acid and the like.

10 In the second invention, at least one of these
monovalent fatty acids is properly mixed and esterified
with pentaerythritol or its condensate to obtain an
ester satisfying desirable physical properties required
for various refrigerators.

15 In order to obtain a sufficiently satisfactory
compatibility with the refrigerant HFC-134a and the
like, it is preferable to use a mixture of straight
chain fatty acid having a carbon number of 3-11,
preferably 5-10 and a branched-chain fatty acid having a
20 carbon number of 3-14, preferably 7-9 as the monovalent
fatty acid. In this case, the amount of the straight or
branched-chain fatty acid used is preferable to be not
less than 50 mol% per the total monovalent fatty acid
used.

25 On the other hand, in order to give a proper
viscosity to the resulting ester, at least one polybasic



acid having a carbon number of 4-36 may be esterified with at least one of pentaerythritol, dipentaerythritol and tripentaerythritol in an amount of not more than 80 mol% per total fatty acid. In this case, the same
05 polybasic acids as described in the first invention are used in the same manner as in the first invention.

The ester compounds according to the second invention can be obtained by the same method as in the first invention.

10 In the esters according to the second invention, the acid value is preferable to be not more than 3 and the hydroxyl value is preferable to be not more than 50 likewise the case of the first invention.

The lubricant for refrigerant HFC-134a and the
15 like according to the third invention comprises an ester obtained by esterifying a polyvalent alcohol represented by the aforementioned general formula (II) with at least one straight or branched-chain monovalent fatty acid having a carbon number of 2-18 and not more than 25 mol%
20 per total fatty acid of at least one polybasic acid having a carbon number of 4-36 as a main component.

When the carbon number of R in the general formula (II) is not less than 4, the compatibility of the resulting ester with HFC-134a and the like is largely
25 lowered. As the polyvalent alcohol, mention may be made of trimethylol ethane, trimethylol propane, trimethylol



butane and the like.

In the third invention, when the carbon number of the monovalent fatty acid is more than 18, it becomes very poor in the compatibility of the resulting synthesized ester with HFC-134a and the like. Particularly, the straight or branched-chain monovalent fatty acids having a carbon number of 3-10 are preferable. As the monovalent fatty acid, mention may be made of the same compounds as described in the second invention.

As to the polybasic acid, the polybasic acid having a carbon number of not more than 3 is a special product and is difficult to be cheaply available and is poor in the stability of the ester after the synthesis. While, when the carbon number exceeds 36, the compatibility of the resulting ester with HFC-134a and the like is largely lowered. Therefore, the carbon number of the polybasic acid is preferable to be 4-36, and particularly the carbon number of 4-10 is favorable for ensuring the compatibility with HFC-134a at a wide range. As the polybasic acid, mention may be made of adipic acid, azelaic acid, sebacic acid and so on. Preferably, the monovalent fatty acid is 2-ethylhexanoic acid, and the polybasic acid is adipic acid.

Moreover, the reason why the amount of the polybasic acid added in the invention is limited to not more than 25 mol% per the total fatty acid is due to the

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fact that when it exceeds 25 mol%, the gelation may be caused and it is difficult to obtain desirable physical properties.

The ester compounds according to the third
05 invention can be obtained by the same method as in the first and second inventions. In any case, it is desirable that the ester does not contain carboxyl group.

The esters according to the invention exhibit a
10 good compatibility with the refrigerant HFC-134a and the like over a wide range of from low temperature to high temperature as a lubricant for use in a refrigerator using HFC-134a as a refrigerant, whereby the lubricity and thermal stability of the refrigeration lubricant can
15 be considerably improved. Furthermore, they are high in the electric insulating property and small in the hygroscopicity as compared with PAG conventionally examined as a refrigeration lubricant for HFC-134a. Therefore, the refrigeration lubricants comprising the
20 ester according to the invention as a main component can solve the problems on the compatibility with HFC-134a and the hygroscopicity, which have never been solved in the conventional technique, and can further enhance the electric insulating property, which comes into problem
25 when HFC-134a is used in a compressor for a refrigerator.



Moreover, additives usually used in the lubricant such as antioxidant, anti-wear agent, epoxy compound and the like may properly be added to the refrigeration lubricant according to the invention.

05 The following examples are given in illustration of the invention and are not intended as limitations thereof.

Examples 1-8, Comparative Examples 1-5

 The performances as a refrigeration lubricant
10 using HFC-134a as a refrigerant were evaluated with respect to eight esters A-1 - A-8 shown in the following Table 1 (all of which esters were not commercially available but were prepared according to the first invention). For the comparison, the same evaluation as
15 mentioned above was made with respect to commercially available PAG (B-1 - B-3, made by Asahi Denka Co., Ltd.) and esters (C-1 - C-2, made by Nippon Oil and Fats Co., Ltd.) as a refrigeration lubricant shown in the following Table 2.

20 The lubricity, compatibility, thermal stability, electric insulating property and hygroscopicity as performances of the refrigeration lubricant for the compressor shown in Tables 1 and 2 were evaluated under the following conditions.

25 Lubricity

 Seizuring load (Falex load-carrying capacity)



was measured according to ASTM D-3233-73 under a controlled atmosphere of HFC-134a blown.

Compatibility

05 After 0.6 g of the test lubricant and 2.4 g of the refrigerant (HFC-134a) were sealed in a glass tube, the cooling at 1°C/min and the heating were carried out, during which a temperature causing two-phase separation was measured.

Thermal stability

10 After 1 g of the test lubricant, 1 g of the refrigerant (HFC-134a or R-12) and a catalyst (wire of iron, copper or aluminum) were sealed in a glass tube, the mixture was heated to 175°C, and a color of the lubricant after 10 days was judged by ASTM color system
15 according to ANSI/ASHRAE 97-1983.

Electric insulating property

It was evaluated by a dielectric constant at 80°C according to JIS C-2101.

Hygroscopicity

20 Into a beaker of 100 ml was charged 60 g of the test lubricant, which was left to stand at a temperature of 25°C and a humidity of 70% for 3 hours and then the water concentration was measured.

The evaluation results are shown in the
25 following Table 3.



Table I

Item Ester	Straight chain fatty acid				Branched-chain fatty acid				Polybasic acid		Dynamic viscosity at 40°C (cSt)	Color (ASTM)
	C ₅	C ₈	C ₁₂	C ₁₈	C ₇	C ₈	C ₉	C ₁₈	adipic acid	sebacic acid		
A-1	30	20	-	-	-	50	-	-	-	-	4.6	L 0.5
A-2	30	-	10	10	50	-	-	-	-	-	7.0	L 0.5
A-3	10	-	-	10	40	-	40	-	-	-	14.4	L 0.5
A-4	-	20	-	-	75	-	-	5	-	-	6.5	L 0.5
A-5	-	5	10	-	-	75	-	-	10	-	11.9	L 0.5
A-6	-	10	-	-	65	-	-	-	-	25	20.9	L 0.5
A-7	-	-	-	-	-	100	-	-	-	-	7.4	L 0.5
A-8	-	10	-	-	40	-	10	-	40	-	22.1	L 0.5

Note) Amount of starting material was represented by mol%.



Table 2

	Type	Trade name	Color (ASTM)	Dynamic viscosity at 40°C (cSt)
B-1	PAG 1	Adekapol M-30 1)	L 0.5	32.8
B-2	PAG 1	Adekapol M-110 2)	L 0.5	105.2
B-3	PAG 1	Adekapol MH-50 3)	L 0.5	54.6
C-1	ester	dioctyl sebacate	L 0.5	11.4
C-2	ester	Unistar MB-816 4)	L 0.5	8.1

- 1) polyoxypropylene glycol monoalkyl ether
- 2) polyoxypropylene glycol monoalkyl ether
- 3) polyoxyethylene propylene glycol monoalkyl ether
- 4) monoester of 2-ethylhexanol and palmitic acid



Table 3

	Test lubricant	Dielectric constant at 80°C (Ω·cm)	Two-phase separation temperature (°C)		Seizuring load (Kgf)	Thermal stability				Hygroscopicity (water content, ppm)
			low temperature	high temperature		refrigerant R-12	refrigerant HFC-134a	color (ASTM)	sludge	
Acceptable Example	A-1	7.5×10^{12}	≤ -50 *	80 ≤ **	510	L 1.0	none	L 1.0	none	320
	A-2	6.1×10^{12}	≤ -50	80 ≤	519	L 1.0	none	L 1.0	none	335
	A-3	4.9×10^{13}	≤ -50	80 ≤	555	L 1.0	none	L 1.0	none	309
	A-4	1.7×10^{13}	≤ -50	80 ≤	541	L 1.0	none	L 1.0	none	317
	A-5	8.0×10^{12}	-45	80 ≤	572	L 1.0	none	L 1.0	none	364
	A-6	5.6×10^{12}	-41	80 ≤	603	L 1.0	none	L 1.0	none	371
	A-7	2.6×10^{13}	≤ -50	80 ≤	569	L 1.0	none	L 1.0	none	315
	A-8	4.8×10^{12}	-36	80 ≤	648	L 1.0	none	L 1.0	none	330
Comparative Example	B-1	2.1×10^7	≤ -50	67	430	8.0 ≤	many	L 1.0	none	1600
	B-2	2.8×10^7	insoluble	insoluble	460	8.0 ≤	many	L 1.0	none	1200
	B-3	≤ 10^7	≤ -50	53	430	8.0 ≤	many	L 1.0	none	2100
	C-1	5.1×10^{12}	insoluble	insoluble	570	L 1.0	none	L 1.0	none	340
	C-2	4.3×10^{12}	insoluble	insoluble	590	L 1.0	none	L 1.0	none	365

* : not higher than -50°C

** : not lower than 80°C

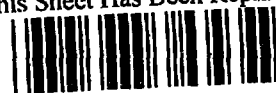


As seen from Table 3, when the esters according to the invention are compared with the conventional PGA (B-1 - B-3), the electric insulating property represented by the dielectric constant is 100,000 times
05 or more and the two-phase separation at a high temperature is not caused. Furthermore, the seizing load is excellent and the hygroscopicity is low. The thermal stability is equal in case of the HFC-134a system, but is considerably excellent in case of the
10 R-12 system. This is very advantageous in practical use because the mixing of HFC-134a and R-12 is not avoided at a stage of replacing the refrigerant from R-12 to HFC-134a.

On the other hand, when the esters according to
15 the invention are compared with the commercially available esters (C-1 - C-2), the two-phase separation temperature is extremely different and the conventional esters are insoluble in HFC-134a. In this point, the molecule designed esters according to the invention have
20 a great merit.

As seen from the above, the esters according to the invention are fairly excellent in the performances as a lubricant as compared with Comparative Examples.
Examples 9-17

25 The performances as a refrigeration lubricant using HFC-134a as a refrigerant were evaluated with



respect to nine esters A-9 - A-17 shown in the following
Table 4 (all of which esters were not commercially
available but were prepared according to the second
invention). The same evaluation as in Example 1 was
05 made to obtain results as shown in the following
Table 5.

10

15

20

25

Table 4

Item Ester	Polyvalent alcohol	Polybasic acid			Dynamic viscosity at 40°C (cSt)	Color (ASTM)
		straight chain fatty acid (mol%)	branched-chain fatty acid (mol%)	polybasic acid (mol%)		
A-9	pentaerythritol	—	isononanoic acid (100)	—	125.4	L 0.5
A-10	pentaerythritol	pentanoic acid (100)	—	—	14.5	L 0.5
A-11	pentaerythritol	propionic acid (70) stearic acid (30)	—	—	33.4	L 0.5
A-12	pentaerythritol	—	2-ethylhexanoic acid (100)	—	42.3	L 0.5
A-13	pentaerythritol	heptanoic acid (15)	isobutanoic acid (75)	adipic acid (10)	110.9	L 0.5
A-14	dipentaerythritol	propionic acid (30)	2-ethylhexanoic acid (70)	—	123.9	L 0.5
A-15	dipentaerythritol	isostearic acid (10)	isobutanoic acid (90)	—	68.4	L 0.5
A-16	dipentaerythritol	butanoic acid (95)	—	sebacic acid (5)	89.4	L 0.5
A-17	tripentaerythritol	propionic acid (20)	2-ethylhexanoic acid (80)	—	146.3	L 0.5

Note) Mol% is an amount per total acid.



Table 5

	Test lubricant	Dielectric constant at 80°C (Ω·cm)	Two-phase separation temperature (°C)		Seizuring load (Kgf)	Thermal stability				Hygroscopicity (water content, ppm)
			low temperature	high temperature		refrigerant R-12	refrigerant HFC-134a	color (ASTM)	sludge	
Acceptable Example	A-9	6.5×10^{13}	-38	80≤	641	L 1.0	none	L 1.0	none	292
	A-10	1.2×10^{13}	≤-50	80≤	524	L 1.0	none	L 1.0	none	319
	A-11	7.6×10^{12}	≤-50	80≤	541	L 1.0	none	L 1.0	none	344
	A-12	1.7×10^{13}	≤-50	80≤	549	L 1.0	none	L 1.0	none	331
	A-13	4.1×10^{12}	-43	80≤	610	L 1.0	none	L 1.0	none	348
	A-14	2.6×10^{12}	-40	80≤	623	L 1.0	none	L 1.0	none	325
	A-15	1.4×10^{13}	≤-50	80≤	581	L 1.0	none	L 1.0	none	339
	A-16	5.1×10^{12}	≤-50	80≤	602	L 1.0	none	L 1.0	none	358
	A-17	4.5×10^{12}	-31	80≤	654	L 1.0	none	L 1.0	none	324

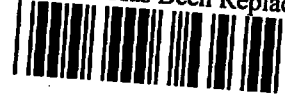


As seen from Table 5, when the esters according to the invention are compared with the conventional PGA (B-1 - B-3) shown in Tables 2 and 3, the electric insulating property represented by the dielectric
05 constant is 100,000 times or more and the two-phase separation at a high temperature is not caused. Furthermore, the seizing load is excellent and the hygroscopicity is low. The thermal stability is equal in case of the HFC-134a system, but is considerably
10 excellent in case of the R-12 system. This is very advantageous in practical use because the mixing of HFC-134a and R-12 is not avoided at a stage of replacing the refrigerant from R-12 to HFC-134a.

On the other hand, when the esters according to
15 the invention are compared with the commercially available esters (C-1 - C-2) shown in Tables 2 and 3, the two-phase separation temperature is extremely different and the conventional esters are insoluble in HFC-134a. In this point, the molecule designed esters
20 according to the invention have a great merit.

As seen from the above, the esters according to the invention are fairly excellent in the performances as a lubricant as compared with Comparative Examples.

The HFC-134a has been mentioned as a possible
25 replacement for R-12 and is used for car air conditioner, refrigerator and the like. Particularly,



in case of the car air conditioner, the compressor is driven in summer season, so that the compatibility between oil and refrigerant at high temperature becomes important. When the two-phase separation between oil
05 and refrigerant is caused in the compressor during the driving, the refrigerant having a larger specific gravity remains in the lower portion of the compressor, resulting in the occurrence of compressor seizing.

In case of the refrigerator, the motor is
10 included in the compressor, so that leakage of electricity comes into problem. In this connection, the esters according to the invention have a dielectric constant higher by 100,000 times or more than that of the conventional PAG and are excellent in the electric
15 insulating property, so that they can be said to be a refrigeration lubricant for the refrigerator.

Concretely, lubricants having a dynamic viscosity of 10-50 cSt at 40°C are used as a lubricant for the refrigerator requiring a two-phase separation
20 temperature of not higher than -40°C, so that the esters A-10, A-11 and A-12 are particularly suitable therefor. On the other hand, lubricants having a dynamic viscosity of 80-150 cSt at 40°C are used as a lubricant for the car air conditioner requiring a two-phase separation
25 temperature of not higher than -20°C, so that the esters



A-9, A-13, A-14, A-16 and A-17 are particularly suitable therefor.

Examples 18-25

The performances as a refrigeration lubricant
05 using HFC-134a as a refrigerant were evaluated with
respect to eight esters A-18 - A-25 shown in the
following Table 6 (all of which esters were not
commercially available but were prepared according to
the third invention). The same evaluation as in
10 Example 1 was made to obtain results as shown in the
following Table 7.

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Table 6

Item Ester	Polyvalent alcohol	Monovalent fatty acid	Polybasic acid	Color (ASTM)	Dynamic viscosity at 40°C (cSt)
A-18	trimethylol ethane	2-ethylhexanoic acid (100)	—	L 0.5	17.9
A-19	trimethylol ethane	2-ethylhexanoic acid (95)	azelaic acid (5)	L _h 0.5	84.1
A-20	trimethylol ethane	2-ethylhexanoic acid (90)	sebacic acid (10)	L 0.5	105.4
A-21	trimethylol ethane	heptanoic acid (100)	—	L 0.5	15.1
A-22	trimethylol ethane	octanoic acid (50) isononanoic acid (50)	—	L 0.5	18.2
A-23	trimethylol ethane	nonanoic acid (70) isononanoic acid (30)	—	L 0.5	20.4
A-24	trimethylol propane	2-ethylhexanoic acid (100)	—	L 0.5	19.1
A-25	trimethylol propane	heptanoic acid (60) 2-ethylhexanoic acid (40)	—	L 0.5	15.4

Note) numerical value in parenthesis is mol% per total fatty acid



Table 7

	Test lubricant	Dielectric constant at 80°C (Ω.cm)	Two-phase separation temperature (°C)		Seizuring load (Kgf)	Thermal stability				Hygroscopicity (water content, ppm)	
			low temperature			high temperature	refrigerant R-12		refrigerant HFC-134a		
							color (ASTM)	sludge	color (ASTM)		sludge
Acceptable Example	A-18	5.6×10^{12}	≤-50	80≤	564	L 1.0	none	L 1.0	none	324	
	A-19	1.9×10^{12}	-30	80≤	612	L 1.0	none	L 1.0	none	368	
	A-20	2.8×10^{12}	-28	80≤	641	L 1.0	none	L 1.0	none	359	
	A-21	7.6×10^{12}	-41	80≤	541	L 1.0	none	L 1.0	none	317	
	A-22	5.9×10^{12}	≤-50	80≤	550	L 1.0	none	L 1.0	none	326	
	A-23	3.1×10^{13}	-38	80≤	581	L 1.0	none	L 1.0	none	333	
	A-24	8.6×10^{12}	≤-50	80≤	534	L 1.0	none	L 1.0	none	319	
	A-25	4.3×10^{12}	≤-50	80≤	519	L 1.0	none	L 1.0	none	321	



As seen from Table 7, when the esters according to the invention are compared with the conventional PGA (B-1 - B-3) shown in Tables 2 and 3, the electric insulating property represented by the dielectric constant is 100,000 times or more and the two-phase separation at a high temperature is not caused. Furthermore, the seizing load is excellent and the hygroscopicity is low. The thermal stability is equal in case of the HFC-134a system, but is considerably excellent in case of the R-12 system.

Recently, HFC-134a causing substantially no breakage of ozone layer is closed up instead of R-12 widely used as a refrigerant in order to cope with the breakage of ozone layer through chlorofluorocarbon and hydrochlorofluorocarbon being a greatest problem in world-wide scale, but is poor in the compatibility with the conventional refrigeration lubricant, which is a bar for the development of replacement system. However, the refrigeration lubricants according to the invention have a sufficient compatibility with HFC-134a as a refrigerant and a high electric insulating property and also are excellent in the total performances, so that they have an effect that the conventional systems can be used as they are even when HFC-134a is used instead of the conventional R-12 and R-22 as a refrigerant.



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1. Use of a lubricant for compressors using a hydrofluorocarbon refrigerant containing no chlorine, comprising as a main component an ester(s) obtained by reacting (a) at least one polyvalent alcohol selected from the group consisting of pentaerythritol, dipentaerythritol and tripentaerythritol with (b) at least one straight chain or branched-chain monovalent saturated fatty acid having a carbon number of 2-18.

2. Use of a lubricant for compressors using a hydrofluorocarbon refrigerant containing no chlorine, comprising as a main component an ester(s) obtained by reacting (a) at least one polyvalent alcohol selected from the group consisting of pentaerythritol, dipentaerythritol and tripentaerythritol with (b) at least one straight chain or branched-chain monovalent saturated fatty acid having a carbon number of 2-18 and (c) at least one saturated polybasic acid having a carbon number of 4-10 in which an amount of said saturated polybasic acid is not more than 80 mol% per total of said monovalent saturated fatty acid and said saturated polybasic acid used.

3. The use according to claim 1^{or claim 2} wherein said monovalent saturated fatty acid is a straight chain monovalent saturated fatty acid having a carbon number of 3-11 and/or a branched-chain monovalent saturated fatty acid having a carbon number of 3-14.



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4. The use according to claim 3, wherein said monovalent saturated fatty acid is a straight chain monovalent saturated fatty acid having a carbon number of 5-10 and/or a branched-chain monovalent saturated fatty acid having a carbon number of 7-9 in which an amount of the branched-chain monovalent saturated fatty acid is not less than 50 mol% per total monovalent saturated fatty acid used.

5. The use according to claim 4, wherein said monovalent saturated fatty acid is selected from the group consisting of pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, decanoic acid, isoheptanoic acid, 2-methylhexanoic acid, 2,2-dimethylpentanoic acid, 2-ethylpentanoic acid, 3-ethylpentanoic acid, 3-methylhexanoic acid, 4-methylhexanoic acid, 5-methylhexanoic acid, isooctanoic acid, 2-methylheptanoic acid, 3-methylheptanoic acid, 4-methylheptanoic acid, 2-ethylhexanoic acid, 2-propylpentanoic acid, 2,2-dimethylhexanoic acid, 2,4-dimethylhexanoic acid, 3,5-dimethylhexanoic acid, 2,2,4-trimethylpentanoic acid, isononanoic acid, 2-methyloctanoic acid, 3-methyloctanoic acid, 2,2-dimethylheptanoic acid, 2-ethylheptanoic acid and 3,5,5-trimethylhexanoic acid.

6. The use according to anyone of claims 1 to 5, wherein said ester has a hydroxyl value of not more than 50, a dielectric constant at 80°C of not less than $10^{12} \Omega \cdot \text{cm}$ and a two-phase separation temperature at low temperature side of not higher than -40°C in the coexistence with said hydrofluorocarbon refrigerant.



7. The use according to anyone of claims 1 to 6, wherein said hydrofluorocarbon refrigerant is 1,1,1,2-tetrafluoroethane.

8. The use according to claim 2, wherein said saturated polybasic acid is selected from the group consisting of succinic acid, glutaric acid, adipic acid, suberic acid, pimelic acid, azelaic acid and sebacic acid.

9. A lubricant for compressors using a hydrofluorocarbon refrigerant containing no chlorine, comprising as a main component an ester(s) obtained by reacting (a) at least one polyvalent alcohol selected from the group consisting of pentaerythritol, dipentaerythritol and tripentaerythritol with (b) at least one straight chain or branched-chain monovalent saturated fatty acid having a carbon number of 2-18.

10. A lubricant for compressors using a hydrofluorocarbon refrigerant containing no chlorine, comprising as a main component an ester(s) obtained by reacting (a) at least one polyvalent alcohol selected from the group consisting of pentaerythritol, dipentaerythritol and tripentaerythritol with (b) at least one straight chain or branched-chain monovalent saturated fatty acid having a carbon number of 2-18 and (c) at least one saturated polybasic acid having a carbon number of 4-10 in which an amount of said saturated polybasic acid is not more than 80 mol% per total of said monovalent saturated fatty acid and said saturated polybasic acid used.

A B S T R A C T

Refrigeration Lubricants

A lubricant comprising
as a main component an ester(s) obtained by reacting (a) at
least one polyvalent alcohol selected from the group consisting
of pentaerythritol, dipentaerythritol and tripentaerythritol
with (b) at least one straight chain or branched-chain
monovalent saturated fatty acid having a carbon number of 2-18.

This lubricant is used for compressors using a
hydrofluorocarbon refrigerant containing no chlorine.

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☒	Claim(s)	: paged 14 to paged 17
☐	Drawing(s)	: paged to paged
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REFRIGERATION LUBRICANTS**Description**

This invention relates to the use of lubricants for compressors using a hydrofluorocarbon refrigerant used with refrigerant and more particularly to lubricants suitable for use in the compression of refrigerants containing no chlorine such as hydrofluorocarbons (HFC), preferably HFC-134a (1,1,1,2-tetrafluoroethane), ~~and the like.~~

Heretofore, compounds containing fluorine and chlorine as a constituent element such as R-11 (trichloromonofluoromethane), R-12 (dichlorodifluoromethane) as a chlorofluorocarbon (CFC), R-22 (monochlorodifluoromethane) as a hydrochlorofluorocarbon (HCFC) ~~and the like~~ have been used as a refrigerant for freezers, air conditioners and refrigerators, ~~and the like.~~ for instance.

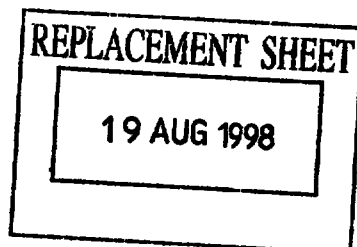
JP-A-56131548 discloses neopentylpolyolesters useful as freon-resisting oil for lubrication.

JP-A-59164393 discloses a refrigerate machine oil which comprises, as base oil, a complex ester synthesized from polyhydric alcohol, 16-18C unsaturated fatty acid and 4-10C dicarboxylic acid. The complex ester has high lubrication and chemical stability and balanced compatibility with freon.

The freons disclosed in the above references are polyhalogenated hydrocarbons containing fluorine and chlorine. In connection with recent problem on breakage of ozone layer, new refrigerants containing no chlorine such as HFC-134a ~~and so on~~ are proposed as a possible replacement for R-12, causing no breakage of ozone layer.

As a refrigeration lubricant, there are known many mineral-series and synthetic oils. However, it has been confirmed that these oils are very poor in the compatibility with HFC-134a and cannot be applied thereto. Therefore, it is important to take a countermeasure on this problem at the present. Furthermore, the lubricity, electric insulating property, energy

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saving property, anti-wear performance, sealability, thermal stability, prevention of sludge formation, and the like are for instance mentioned as performances required in the refrigeration lubricant, so that they are required to be considered in the development of the above countermeasure.

Incidentally, there have hitherto been known polyether series synthetic lubricants as a synthetic oil, which are reported in Journal of the Oil Chemistry, vol. 29, No. 9, pp 336-343 (1980) and Journal of the Petroleum Technology, vol. 8, No. 6, pp 562-566 (1985). Furthermore, Japanese Patent laid open No. 61-281199 describes a mixture of polyglycol represented by a general formula of $R_1[O-(R_2O)_m-R_3]_n$, an alkylbenzene and the like, and Japanese Patent laid open No. 57-63395 describes an oil obtained by mixing a polyether such as high molecular weight polyoxypropylene monobutyl ether with an epoxycycloalkyl compound, and Japanese Patent laid open No. 59-117590 describes a high viscosity mixed oil of a polyether compound and a paraffinic or naphthanic mineral oil.

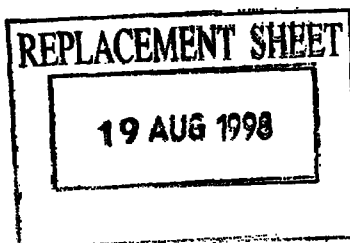
However, the conventional synthetic lubricants as mentioned above cannot be a refrigeration lubricant using HFC-134a as a refrigerant from a viewpoint of compatibility, and the like. for instance.

In US Patent No. 4,755,316, polyoxyalkylene glycol (hereinafter abbreviated as PAG) having hydroxyl groups (-OH) at both terminals is reported as a refrigeration lubricant using HFC-134a. Further, it is described that PAG is dissolved in HFC-134a within a wide temperature range as compared with general PAG containing hydroxyl group and alkyl group at its terminals, whereby the recycle of the lubricant into a compressor is improved in the refrigeration system and the seizing in the actuation of the compressor at high temperature is prevented. Moreover, the temperature range compatible with HFC-134a is described to be between -40°C and +50°C.

On the contrary, HFC-134a is a replacing refrigerant of R-12 and is mainly expected for use in a car air conditioner a or refrigerator, and the like, for instance. In case of the refrigerator, it is required to have a good compatibility between lubricant and refrigerant, and further the lubricant itself is necessary to have an electric insulating property because the motor is

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5 substantially existent in the refrigeration system. However, the conventional compounds examined as a lubricant for HFC-134a refrigerant inclusive of PAG disclosed in US Patent No. 4,755,316 are remarkably poor in the electric insulating property as compared with the conventional refrigeration mineral oil and high in the hygroscopicity.

10 It is, ~~therefore,~~ an object of the invention to provide a refrigeration lubricant, ~~having an~~ which has excellent compatibility with a new refrigerant such as HFC-134a or the like within a wide temperature range, a high electric insulating property and a low hygroscopicity, for compressors using a hydrofluorocarbon refrigerant containing no chlorine.

15 At the present, a part of commercially available esters is used in systems using refrigerants R-12, R-22, ~~and the like,~~ but is incompatible with HFC-134a as a new refrigerant or is very narrow in the compatible range therewith. In this connection, the inventors have aimed at the fact that the ester has a high electric insulating property, a low hygroscopicity, a good lubricity and a high stability as compared with PAG and made various studies with respect to the molecule design of the ester showing a wide range of compatibility with HFC-134a, and found that only esters having a considerably restricted structure can be used in the HFC-134a refrigeration system, and as a result, the invention has been accomplished.

20 [^] The present invention refers to the use of a lubricant for compressors using a hydrofluorocarbon refrigerant containing no chlorine, comprising as a main component an ester(s) obtainable by reacting (a) at least one polyvalent alcohol selected from the group consisting of pentaerythritol, dipentaerythritol and tripentaerythritol with (b) a mixture of at least one of straight chain monovalent fatty acids having a carbon number of 3-11 and at least one of branched-chain monovalent fatty acids having a carbon number of 4-14, wherein the amount of the branched-chain monovalent fatty acid is not less than 50 mol% per total monovalent fatty acid used.

25 [^] Furthermore, the present invention refers to the use of a lubricant for compressors using a hydrofluorocarbon refrigerant containing no chlorine, comprising as a main component an ester(s) obtainable by reacting (a) at least one polyvalent alcohol selected from the group consisting of

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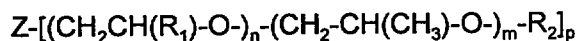


pentaerythritol, dipentaerythritol and tripentaerythritol with (b) a mixture of at least one of straight chain monovalent fatty acids having a carbon number of 3-11 and at least one of branched-chain monovalent fatty acids having a carbon number of 4-14, wherein the amount of the branched-chain monovalent fatty acid is not less than 50 mol% per total monovalent fatty acid used, and (c) at least one polybasic acid having a carbon number of 4-10, wherein the amount of the polybasic acid is not more than 80 mol% per total fatty acid.

The present invention also refers to the use of a lubricant for compressors using a hydrofluorocarbon refrigerant containing no chlorine, comprising as a main component an esters(s) obtainable by reacting (a) at least one polyvalent alcohol selected from pentaerythritol and dipentaerythritol, with (b) at least one branched-chain monovalent fatty acid selected from isobutanoic acid, isopentanoic acid, isoheptanoic acid and isononanoic acid.

The present application also refers to the use of a lubricant for compressors using a hydrofluorocarbon refrigerant containing no chlorine comprising as a main component (an) ester(s) obtainable by reacting (a) at least one polyvalent alcohol selected from pentaerythritol and dipentaerythritol, with (b) at least one branched-chain monovalent fatty acid having a carbon number of 4 to 18, with the proviso that

- i) said lubricant does not contain a polyether polyol in an amount of 5 to 95 weight percent according to the general formula



wherein

Z is the residue of a compound having 1 to 8 active hydrogens,

R₁ is hydrogen, ethyl or mixtures thereof n is 0 or a positive number,

m is a positive number,

n+m is a number having a value which will give a polyether polyol with a number average molecular weight range from about 400 to



about 5000,

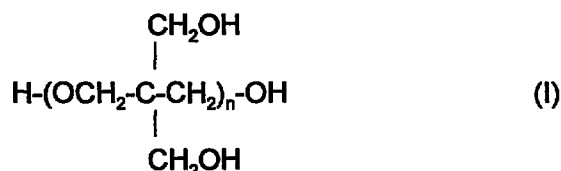
R_2 is hydrogen or an alkyl group of 1 to 6 carbon atoms,

p is an integer having a value equal to the number of active hydrogens of Z ,

and

ii) said lubricant is not used in a liquid composition comprising a major amount (more than 50% by weight) of a fluorine containing hydrocarbon refrigerant and a minor amount of (less than 50% by weight) of said lubricant.

Pentaerythritol, dipentaerythritol and tripentaerythritol are represented by the following formula (I) :



(in which n is 1, 2 or 3).

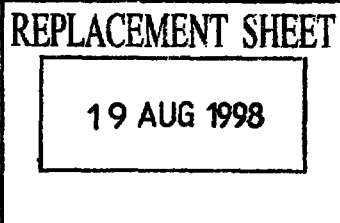
In a preferred embodiment of the invention, the hydrofluorocarbon refrigerant is 1,1,1,2-tetrafluoroethane (HFC-134a).

In the condensate of pentaerythritol, the polymerization degree may be determined in accordance with the viscosity required in the resulting synthesized ester.

As the monovalent fatty acid, mention may be made of propionic acid, butanoic acid, isobutanoic acid, pentanoic acid, isopentanoic acid, hexanoic acid, heptanoic acid, isoheptanoic acid, octanoic acid, 2-ethyl hexanoic acid, nonanoic acid, 3,5,5-trimethyl hexanoic acid, decanoic acid, and undecanoic acid.

~~In the first invention, at least one of branched-chain monovalent fatty acids these monovalent fatty acids is properly esterified with neopentyl-glycol~~ having a carbon number of 4-18 or a mixture of at least one of straight-chain monovalent fatty acids having a carbon number of 3-11 and at least one of branched-chained monovalent fatty acids having a carbon





number of 4-14, is properly mixed and esterified with pentaerythritol or its condensate to obtain an ester satisfying desirable physical properties required for various refrigerators.

5 In order to obtain a sufficiently satisfactory compatibility with the refrigerant HFC-134a and the like, ~~it is preferable to use a mixture of straight chain fatty acid having a carbon number of 3-11, preferably 5-10 and a branched-chain fatty acid having a carbon number of 3-14, preferably 5-10 and a 7-9 as the monovalent fatty acid. In this case, the amount of the~~
10 ~~straight or branched-chain fatty acid used is preferable to be not less than 50 mol% per the total~~ having a carbon number 4-14, preferably 7-9 as the monovalent fatty acid can be used.

In this case, the amount of the branched-chain fatty acid used is not less than 50 mol% per the total monovalent fatty acid used.

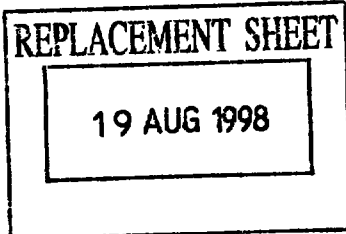
15 ~~According to the invention,~~ On the other hand, in order to give a proper viscosity to the resulting ester, at least one polybasic acid having a carbon number of ~~4-36~~ 4-10 may be esterified with at least one of pentaerythritol, dipentaerythritol and tripentaerythritol in an amount of not more than 80 mol% per total fatty acid. In this case the following polybasic
20 acids are used : succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, phthalic acid, maleic acid and trimellitic acid.

[^] The ester compounds ~~according to the first~~ used in the present invention can be obtained by the esterification reaction through dehydration reaction between the specified polyvalent alcohol and the specified fatty acid as mentioned above, or the general esterification reaction through an acid
25 anhydride, an acid chloride or the like as a derivative of the fatty acid.

[^] In the esters used in the present invention, the acid value is preferable to be not more than 3 mg KOH/g and the hydroxyl value is preferable to be not more than 50 mg KOH/g.

[^] The esters ~~according to~~ used in the invention exhibit a good compatibility with the refrigerant HFC-134a and the like over a wide range of from low temperature to high temperature as a lubricant for use in a refrigerator using HFC-134a as a refrigerant, whereby the lubricity and thermal stability of the refrigeration lubricant can be considerably improved.





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Furthermore, they are high in the electric insulating property and small in the hygroscopicity as compared with PAG conventionally examined as a refrigeration lubricant for HFC-134a. Therefore, by the used the-refrigeration lubricants comprising the ester according to-used in the invention as a main component ~~can solve~~ the problems on the compatibility with HFC-134a and the hygroscopicity, which have never been solved in the conventional technique, can be solved and the electric insulating property, which comes into problem when HFC-134a is used in a compressor for a refrigerator, can be further enhanced.

Moreover, additives usually used in the lubricant such as antioxidant, anti-wear agent, epoxy compound, ~~and the like~~ for instance may properly be added to the refrigeration lubricant used in-according-to the invention.

Examples 1-6

The performances as a refrigeration lubricant using HFC-134a as a refrigerant were evaluated with respect to ~~eight~~ six esters A-1 - A-6 shown in the following Table 1 (all of which esters were not commercially available but were prepared according to the first invention). For the comparison, the same evaluation as mentioned above was made with respect to commercially available PAG (B-1 - B-3, made by Asahi Denka Co., Ltd.) and esters (C-1 - C-2, made by Nippon Oil and Fats Co., Ltd.) as a refrigeration lubricant shown in the following Table 2.

The lubricity, compatibility, thermal stability, electric insulating property and hygroscopicity as performances of the refrigeration lubricant for the compressor shown in Tables 1 and 2 were evaluated under the following conditions.

Lubricity

Seizuring load (Falex load-carrying capacity) was measured according to ASTM D-3233-73 under a controlled atmosphere of HFC-134a blown.

Compatibility

After 0.6 g of the test lubricant and 2.4 g of the refrigerant (HFC-134a) were sealed in a glass tube, the cooling at 1°C/min and the heating

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were carried out, during which a temperature causing two-phase separation was measured.

Thermal stability

After 1 g of the test lubricant, 1 g of the refrigerant (HFC-134a or R-12) and a catalyst (wire of iron, copper or aluminium) were sealed in a glass tube, the mixture was heated to 175°C, and a color of the lubricant after 10 days was judged by ASTM color system according to ANSI/ASHRAE 97-1983.

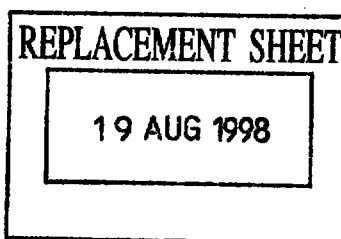
Electric insulating property

It was evaluated by a dielectric constant at 80°C according to JIS C-2101.

Hygroscopicity

Into a beaker of 100 ml was charged 60 g of the test lubricant, which was left to stand at a temperature of 25°C and a humidity of 70% for 3 hours and then the water concentration was measured.

The evaluation results are shown in the following Table 3.



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Table 1

Item Ester	Polyvalent alcohol	Polybasic acid			Dynamic viscosity at 40°C (cSt) mm ² /s	Color (ASTM)
		straight chain fatty acid (mol%)	branched-chain fatty acid (mol%)	polybasic acid (mol%)		
A-1	pentaerythritol	—	isononanoic acid (100)	—	125.4	L 0.5
A-2	pentaerythritol	—	2-ethylhexanoic acid (100)	—	42.3	L 0.5
A-3	pentaerythritol	heptanoic acid (15)	isobutanoic acid (75)	adipic acid (10)	110.9	L 0.5
A-4	dipentaerythritol	propionic acid (30)	2-ethylhexanoic acid (70)	—	123.9	L 0.5
A-5	dipentaerythritol	—	isobutanoic acid (90) isostearic acid (10)	—	68.	L 0.5
A-6	tripentaerythritol	propionic acid (20)	2-ethylhexanoic acid (80)	—	146.3	L 0.5

Note) Mol% is an amount per total acid.

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Table 2

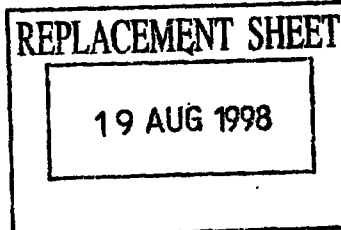
	Type	Trade name	Color (ASTM)	Dynamic viscosity at 40°C (cSt) mm^2/s
B-1	PAG 1	Adekapol M-30 1)	L 0.5	32.8
B-2	PAG 1	Adekapol M-110 2)	L 0.5	105.2
B-3	PAG 1	Adekapol MH-50 3)	L 0.5	54.6
C-1	ester	dioctyl sebacate	L 0.5	11.4
C-2	ester	Unistar MB-816 4)	L 0.5	8.1

1) polyoxypropylene glycol monoalkyl ether

2) polyoxypropylene glycol monoalkyl ether

3) polyoxyethylene propylene glycol monoalkyl ether

4) monoester of 2-ethylhexanol and palmitic acid



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Table 3

Test lubricant used in the invention	Dielectric constant at 80°C (Ω.cm)	Two-phase separation temperature (°C)		Seizuring load (Kgf)	Thermal stability				Hygroscopicity (water content, ppm)
					refrigerant R-12		refrigerant HFC-134a		
		low temperature	high temperature		color (ASTM)	sludge	color (ASTM)	sludge	
A-1	6.5×10^{13}	-38	80≤	641	L 1.0	none	L 1.0	none	292
A-2	1.7×10^{13}	≤-50	80≤	549	L 1.0	none	L 1.0	none	331
A-3	4.1×10^{12}	-43	80≤	610	L 1.0	none	L 1.0	none	348
A-4	2.6×10^{12}	-40	80≤	623	L 1.0	none	L 1.0	none	325
A-5	1.4×10^{13}	≤-50	80≤	581	L 1.0	none	L 1.0	none	339
A-6	4.5×10^{12}	-31	80≤	654	L 1.0	none	L 1.0	none	324

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Table 3 (Continue)

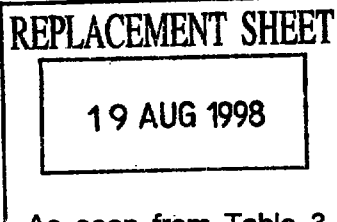
Test lubricant used for comparison	Dielectric constant at 80°C (Ω-cm)	Two-phase separation temperature (°C)		Seizuring load (Kgf)	Thermal stability				Hygroscopicity (water content, ppm)
		low temperature	high temperature		refrigerant R-12		refrigerant HFC-134a		
					color (ASTM)	sludge	color (ASTM)	sludge	
B-1	2.1×10^7	≤-50	67	430	8.0≤	many	L 1.0	none	1600
B-2	2.8×10^7	insoluble	insoluble	460	8.0≤	many	L 1.0	none	1200
B-3	≤10 ⁷	≤-50	53	430	8.0≤	many	L 1.0	none	2100
C-1	5.1×10^{12}	insoluble	insoluble	570	L 1.0	none	L 1.0	none	340
C-2	4.3×10^{12}	insoluble	insoluble	590	L 1.0	none	L 1.0	none	365

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5 ~~As seen from Table 3,~~ when the esters ~~according to~~ used in the invention are compared with the conventional PGA (B-1 - B-3) used for comparison shown in Tables 2 and 3, the electric insulating property represented by the dielectric constant is 100,000 times or more and the two-phase separation at a high temperature is not caused. Furthermore, the seizing load is excellent and the hygroscopicity is low. The thermal stability is equal in case of the HFC-134a system, but is considerably excellent in case of the R-12 system. This is very advantageous in practical use because the mixing of HFC-134a and R-12 is not avoided at a stage of replacing the refrigerant from R-12 to HFC-134a.

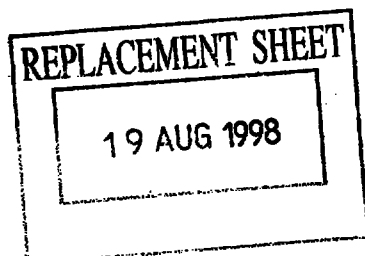
10 On the other hand, when the esters ~~according to~~ used in the invention are compared with the commercially available esters (C-1 - C-2) used for comparison shown in Tables 2 and 3, the two-phase separation temperature is extremely different and the conventional esters are insoluble in HFC-134a. In this point, the molecule designed esters ~~according to~~ used in the invention have a great merit.

15 As seen from the above, the esters ~~according to~~ used in the invention are fairly excellent in the performances as a lubricant as compared with ~~Comparative Examples~~ those used for comparison.

20 The HFC-134a has been mentioned as a possible replacement for R-12 and is used for car air conditioner and refrigerator, ~~and the like.~~ for instance. Particularly, in case of the car air conditioner, the compressor is driven in summer season, so that the compatibility between oil and refrigerant at high temperature becomes important. When the two-phase separation between oil and refrigerant is caused in the compressor during the driving, the refrigerant having a larger specific gravity remains in the lower portion of the compressor, resulting in the occurrence of compressor seizing.

25 In case of the refrigerator, the motor is included in the compressor, so that leakage of electricity comes into problem. In this connection, the esters ~~according to~~ used in the invention have a dielectric constant higher by 100,000 times or more than that of the conventional PAG and are excellent in the electric insulating property, so that they can be said to be





refrigeration lubricant for the refrigerator.

Concretely, lubricants having a dynamic viscosity of 10-50 mm^2/s (cSt) at 40°C are used as a lubricant for the refrigerator requiring a two-phase separation temperature of not higher than -40°C, so that the esters A-2 is particularly suitable therefor. On the other hand, lubricants having a dynamic viscosity of 80-150 mm^2/s (cSt) at 40°C are used as a lubricant for the car air conditioner requiring a two-phase separation temperature of not higher than -20°C, so that the esters A-1, A-3, A-4, and A-6 are particularly suitable therefor.

Recently, HFC-134a causing substantially no breakage of ozone layer is closed up instead of R-12 widely used as a refrigerant in order to cope with the breakage of ozone layer through chlorofluorocarbon and hydrochlorofluorocarbon being a greatest problem in world-wide scale, but is poor in the compatibility with the conventional refrigeration lubricant, which is a bar for the development of replacement system. However, the refrigeration lubricants ~~according to~~ used in the invention have a sufficient compatibility with HFC-134a as a refrigerant and a high electric insulating property and also are excellent in the total performances, so that they have the effect that the conventional systems can be used as they are even when HFC-134a is used instead of the conventional R-12 and R-22 as a refrigerant.

Claims

1. Use of a lubricant for compressors using a hydrofluorocarbon refrigerant containing no chlorine, comprising as a main component an ester(s) obtainable by reacting (a) at least one polyvalent alcohol selected from the group consisting of pentaerythritol, dipentaerythritol and tripentaerythritol with (b) a mixture of at least one of straight chain monovalent fatty acids having a carbon number of 3-11 with at least one of branched-chain monovalent fatty acids having a carbon number of 4-14, wherein the amount of the branched-chain monovalent fatty acid is not less than 50 mol% per total monovalent fatty acid used. ~~or branched-chain monovalent saturated fatty acid having a carbon number of 2-18.~~



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2. ~~The use~~ Use of a lubricant according to Claim 1, wherein said straight chain monovalent fatty acid is selected from the group consisting of propionic acid, butanoic acid, pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, decanoic acid and undecanoic acid, and said branched-chain monovalent fatty acid is selected from the group consisting of isobutanoic acid, isopentanoic acid, isoheptanoic acid, 2-ethylhexanoic acid and 3,5,5-trimethylhexanoic acid.
3. Use of a lubricant according to claim 1, wherein said branched-chain monovalent fatty acid is one having a carbon number of 7-9.
4. Use of a lubricant according to any one of claims 1 to 3, wherein said ester has a total acid value of not more than 3 mgKOH/g and a hydroxyl value of not more than 50 mgKOH/g.
5. ~~The use~~ Use of a lubricant according any one of claims 1 to ~~6~~4, wherein said hydrofluorocarbon refrigerant is 1,1,1,2-tetrafluoroethane.
6. ~~A Use of a~~ Use of a lubricant for compressors using a hydrofluorocarbon refrigerant containing no chlorine, comprising as a main component an ester(s) ~~obtained~~ obtainable by reacting (a) at least one polyvalent alcohol selected from the group consisting of pentaerythritol, dipentaerythritol and tripentaerythritol with (b) a mixture of at least one of straight chain monovalent fatty acids having a carbon number of 3-11 with at least one of branched-chain monovalent fatty acids having a carbon number of 4-14, wherein the amount of the branched-chain monovalent fatty acid is not less than 50 mol% per total monovalent fatty acid used, and (c) at least one polybasic acid having a carbon number of 4-10, wherein the amount of the polybasic acid is not more than 80 mol% per total fatty acid.
7. Use of a lubricant according to claim 6, wherein said straight chain monovalent fatty acid is selected from the group consisting of propionic acid, butanoic acid, pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, decanoic acid and undecanoic acid, and said branched-chain monovalent fatty acid is

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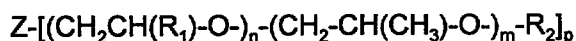
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selected from the group consisting of isobutanoic acid, isopentanoic acid, isoheptanoic acid, 2-ethylhexanoic acid and 3,5,5-trimethylhexanoic acid.

- 5 8. Use of a lubricant according to claim 6, wherein said polybasic acid is selected from the group consisting of succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid and sebacic acid.
9. Use of a lubricant according to any one of claims 6 to 8, wherein said ester has a total acid value of not more than 3 mgKOH/g and a hydroxyl value of not more than 50 mgKOH/g.
- 10 10. Use of a lubricant according to any one of claims 6 to 9, wherein said hydrofluorocarbon refrigerant is 1,1,1,2-tetrafluoroethane.
11. Use of a lubricant for compressors using a hydrofluorocarbon refrigerant containing no chlorine, said lubricant comprising as a main component (an) ester(s) obtainable by reacting (a) at least one polyvalent alcohol selected from pentaerythritol and dipentaerythritol, with (b) at least one branched-chain monovalent fatty acid selected from isobutanoic acid, isopentanoic acid, isoheptanoic acid and isononanoic acid.
- 15 12. Use of a lubricant according to claim 11, wherein said polyvalent alcohol is pentaerythritol.
- 20 13. Use of a lubricant for compressors using a hydrofluorocarbon refrigerant containing no chlorine, said lubricant comprising as a main component (an) ester(s) obtainable by reacting (a) at least one polyvalent alcohol selected from pentaerythritol and dipentaerythritol, with (b) at least one branched-chain monovalent fatty acid having a carbon number of 4 to 18, with the proviso that
 - i) said lubricant does not contain a polyether polyol in an amount of 5 to 95 weight percent according to the general formula
- 25



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wherein

Z is the residue of a compound having 1 to 8 active hydrogens,

R_1 is hydrogen, ethyl or mixtures thereof

n is 0 or a positive number,

m is a positive number,

$n+m$ is a number having a value which will give a polyether polyol with a number average molecular weight range from about 400 to about 5000,

R_2 is hydrogen or an alkyl group of 1 to 6 carbon atoms,

p is an integer having a value equal to the number of active hydrogens of Z,

and

ii) said lubricant is not used in a liquid composition comprising a major amount (more than 50% by weight) of a fluorine containing hydrocarbon refrigerant and a minor amount of (less than 50% by weight) of said lubricant.

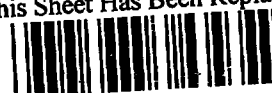
14. Use of a lubricant according to claim 13, wherein said polyvalent alcohol is pentaerythritol.

15. Use of a lubricant according to claim 13 or 14, wherein said branched-chain monovalent fatty acid is selected from the group consisting of isobutanoic acid, isopentanoic acid, isoheptanoic acid, 2-ethylhexanoic acid, isononanoic acid and 3,5,5-trimethylhexanoic acid.

16. Use of a lubricant according to Claim 13 or 14, wherein said branched-chain monovalent fatty acid is one having a carbon number of 7-9.

17. Use of a lubricant according to claim 16, wherein said branched-chain monovalent fatty acid is selected from the group consisting of isoheptanoic acid, 2-ethylhexanoic acid, isononanoic acid and 3,5,5-trimethylhexanoic acid.

18. Use of a lubricant according to any one of claims 11 to 17, wherein said hydrofluorocarbon refrigerant is 1,1,1,2-tetrafluoroethane.



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- ☒ Description : paged .1. to paged .14.
☒ Claim(s) : paged .15. to paged .18.
☐ Drawing(s) : paged to paged
☐ Abstract : paged to paged

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REFRIGERATION LUBRICANTS

DATE OF RECEIPT 29/10/99

Description

This invention relates to the use of lubricants for compressors using
a hydrofluorocarbon refrigerant used with refrigerant and more particularly
~~to lubricants suitable for use in the compression of refrigerants~~ containing no
 chlorine such as hydrofluorocarbons (HFC), preferably HFC-134a (1,1,1,2-
 tetrafluoroethane). ~~and the like.~~

Heretofore, compounds containing fluorine and chlorine as a
 constituent element such as R-11 (trichloromonofluoromethane), R-12
 (dichlorodifluoromethane) as a chlorofluorocarbon (CFC), R-22
 (monochlorodifluoromethane) as a hydrochlorofluorocarbon (HCFC) ~~and the~~
~~like~~ have been used as a refrigerant for freezers, air conditioners and
 refrigerators, ~~and the like.~~ for instance.

JP-A-56131548 discloses neopentylpolyolesters useful as freon-
 resisting oil for lubrication.

JP-A-59164393 discloses a refrigerate machine oil which comprises,
 as base oil, a complex ester synthesized from polyhydric alcohol, 16-18C
 unsaturated fatty acid and 4-10C dicarboxylic acid. The complex ester has
 high lubrication and chemical stability and balanced compatibility with freon.

The freons disclosed in the above references are polyhalogenated
hydrocarbons containing fluorine and chlorine. In connection with recent
 problem on breakage of ozone layer, new refrigerants containing no chlorine
 such as HFC-134a ~~and so on~~ are proposed as a possible replacement for
 R-12, causing no breakage of ozone layer.

As a refrigeration lubricant, there are known many mineral-series and
 synthetic oils. However, it has been confirmed that these oils are very poor
 in the compatibility with HFC-134a and cannot be applied thereto. Therefore,
 it is important to take a countermeasure on this problem at the present.
 Furthermore, the lubricity, electric insulating property, energy

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saving property, anti-wear performance, sealability, thermal stability, prevention of sludge formation, ~~and the like are for instance~~ mentioned as performances required in the refrigeration lubricant, so that they are required to be considered in the development of the above countermeasure.

Incidentally, there have hitherto been known polyether series synthetic lubricants as a synthetic oil, which are reported in Journal of the Oil Chemistry, vol. 29, No. 9, pp 336-343 (1980) and Journal of the Petroleum Technology, vol. 8, No. 6, pp 562-566 (1985). Furthermore, Japanese Patent laid open No. 61-281199 describes a mixture of polyglycol represented by a general formula of $R_1[O-(R_2O)_m-R_3]_n$, an alkylbenzene and the like, and Japanese Patent laid open No. 57-63395 describes an oil obtained by mixing a polyether such as high molecular weight polyoxypropylene monobutyl ether with an epoxycycloalkyl compound, and Japanese Patent laid open No. 59-117590 describes a high viscosity mixed oil of a polyether compound and a paraffinic or naphthanic mineral oil.

However, the conventional synthetic lubricants as mentioned above cannot be a refrigeration lubricant using HFC-134a as a refrigerant from a viewpoint of compatibility, ~~and the like~~. for instance.

In US Patent No. 4,755,316, polyoxyalkylene glycol (hereinafter abbreviated as PAG) having hydroxyl groups (-OH) at both terminals is reported as a refrigeration lubricant using HFC-134a. Further, it is described that PAG is dissolved in HFC-134a within a wide temperature range as compared with general PAG containing hydroxyl group and alkyl group at its terminals, whereby the recycle of the lubricant into a compressor is improved in the refrigeration system and the seizing in the actuation of the compressor at high temperature is prevented. Moreover, the temperature range compatible with HFC-134a is described to be between -40°C and +50°C.

On the contrary, HFC-134a is a replacing refrigerant of R-12 and is mainly expected for use in a car air conditioner ~~a or refrigerator, and the like~~. for instance. In case of the refrigerator, it is required to have a good compatibility between lubricant and refrigerant, and further the lubricant itself is necessary to have an electric insulating property because the motor is

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substantially existent in the refrigeration system. However, the conventional compounds examined as a lubricant for HFC-134a refrigerant inclusive of PAG disclosed in US Patent No. 4,755,316 are remarkably poor in the electric insulating property as compared with the conventional refrigeration mineral oil and high in the hygroscopicity.

It is ~~therefore~~ an object of the invention to provide a refrigeration lubricant, ~~having an~~ which has excellent compatibility with a new refrigerant such as HFC-134a or the like within a wide temperature range, a high electric insulating property and a low hygroscopicity, for compressors using a hydrofluorocarbon refrigerant containing no chlorine.

At the present, a part of commercially available esters is used in systems using refrigerants R-12, R-22, ~~and the like~~, but is incompatible with HFC-134a as a new refrigerant or is very narrow in the compatible range therewith. In this connection, the inventors have aimed at the fact that the ester has a high electric insulating property, a low hygroscopicity, a good lubricity and a high stability as compared with PAG and made various studies with respect to the molecule design of the ester showing a wide range of compatibility with HFC-134a, and found that only esters having a considerably restricted structure can be used in the HFC-134a refrigeration system, and as a result, the invention has been accomplished.

The present invention refers to the use of a lubricant for compressors using a hydrofluorocarbon refrigerant containing no chlorine, comprising as a main component an ester(s) obtainable by reacting (a) at least one polyvalent alcohol selected from the group consisting of pentaerythritol, dipentaerythritol and tripentaerythritol with (b) a mixture of at least one of straight chain monovalent fatty acids having a carbon number of 3-11 and at least one of branched-chain monovalent fatty acids having a carbon number of 4-14, wherein the amount of the branched-chain monovalent fatty acid is not less than 50 mol% per total monovalent fatty acid used.

Furthermore, the present invention refers to the use of a lubricant for compressors using a hydrofluorocarbon refrigerant containing no chlorine, comprising as a main component an ester(s) obtainable by reacting (a) at least one polyvalent alcohol selected from the group consisting of

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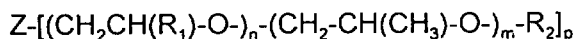
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pentaerythritol, dipentaerythritol and tripentaerythritol with (b) a mixture of at least one of straight chain monovalent fatty acids having a carbon number of 3-11 and at least one of branched-chain monovalent fatty acids having a carbon number of 4-14, wherein the amount of the branched-chain monovalent fatty acid is not less than 50 mol% per total monovalent fatty acid used, and (c) at least one polybasic acid having a carbon number of 4-10, wherein the amount of the polybasic acid is not more than 80 mol% per total fatty acid.

The present invention also refers to the use of a lubricant for compressors using a hydrofluorocarbon refrigerant containing no chlorine, comprising as a main component an esters(s) obtainable by reacting (a) at least one polyvalent alcohol selected from pentaerythritol and dipentaerythritol, with (b) at least one branched-chain monovalent fatty acid selected from isobutanoic acid, isopentanoic acid, isoheptanoic acid and isononanoic acid.

The present application also refers to the use of a lubricant for compressors using a hydrofluorocarbon refrigerant containing no chlorine comprising as a main component (an) ester(s) obtainable by reacting (a) at least one polyvalent alcohol selected from pentaerythritol and dipentaerythritol, with (b) at least one branched-chain monovalent fatty acid having a carbon number of 4 to 18, with the proviso that

- i) said lubricant does not contain a polyether polyol in an amount of 5 to 95 weight percent according to the general formula



wherein

Z is the residue of a compound having 1 to 8 active hydrogens,

R₁ is hydrogen, ethyl or mixtures thereof n is 0 or a positive number, m is a positive number,

n+m is a number having a value which will give a polyether polyol with a number average molecular weight range from about 400 to

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about 5000,

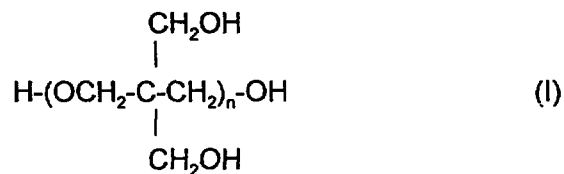
R_2 is hydrogen or an alkyl group of 1 to 6 carbon atoms,

p is an integer having a value equal to the number of active hydrogens of Z ,

and

ii) said lubricant is not used in a liquid composition comprising a major amount (more than 50% by weight) of a fluorine containing hydrocarbon refrigerant and a minor amount of (less than 50% by weight) of said lubricant.

Pentaerythritol, dipentaerythritol and tripentaerythritol are represented by the following formula (I) :



(in which n is 1, 2 or 3).

In a preferred embodiment of the invention, the hydrofluorocarbon refrigerant is 1,1,1,2-tetrafluoroethane (HFC-134a).

In the condensate of pentaerythritol, the polymerization degree may be determined in accordance with the viscosity required in the resulting synthesized ester.

As the monovalent fatty acid, mention may be made of propionic acid, butanoic acid, isobutanoic acid, pentanoic acid, isopentanoic acid, hexanoic acid, heptanoic acid, isoheptanoic acid, octanoic acid, 2-ethyl hexanoic acid, nonanoic acid, 3,5,5-trimethyl hexanoic acid, decanoic acid, and undecanoic acid.

~~In the first invention, at least one of branched-chain monovalent fatty acids these monovalent fatty acids is properly esterified with neopentyl glycol~~ having a carbon number of 4-18 or a mixture of at least one of straight-chain monovalent fatty acids having a carbon number of 3-11 and at least one of branched-chained monovalent fatty acids having a carbon

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number of 4-14, is properly mixed and esterified with pentaerythritol or its condensate to obtain an ester satisfying desirable physical properties required for various refrigerators.

5 In order to obtain a sufficiently satisfactory compatibility with the refrigerant HFC-134a and the like, ~~it is preferable to use a mixture of straight chain fatty acid having a carbon number of 3-11, preferably 5-10 and a branched-chain fatty acid having a carbon number of 3-14, preferably 5-10 and a 7-9 as the monovalent fatty acid. In this case, the amount of the~~
10 ~~straight or branched-chain fatty acid used is preferable to be not less than 50 mol% per the total having a carbon number 4-14, preferably 7-9 as the monovalent fatty acid can be used.~~

In this case, the amount of the branched-chain fatty acid used is not less than 50 mol% per the total monovalent fatty acid used.

15 ~~According to the invention,~~ On the other hand, in order to give a proper viscosity to the resulting ester, at least one polybasic acid having a carbon number of ~~4-36~~ 4-10 may be esterified with at least one of pentaerythritol, dipentaerythritol and tripentaerythritol in an amount of not more than 80 mol% per total fatty acid. In this case the following polybasic
20 acids are used : succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, phthalic acid, maleic acid and trimellitic acid.

The ester compounds ~~according to the first~~ used in the present invention can be obtained by the esterification reaction through dehydration reaction between the specified polyvalent alcohol and the specified fatty acid as mentioned above, or the general esterification reaction through an acid
25 anhydride, an acid chloride or the like as a derivative of the fatty acid.

In the esters used in the present invention, the acid value is preferable to be not more than 3 mg KOH/g and the hydroxyl value is preferable to be not more than 50 mg KOH/g.

The esters ~~according to~~ used in the invention exhibit a good compatibility with the refrigerant HFC-134a and the like over a wide range of from low temperature to high temperature as a lubricant for use in a refrigerator using HFC-134a as a refrigerant, whereby the lubricity and thermal stability of the refrigeration lubricant can be considerably improved.

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Furthermore, they are high in the electric insulating property and small in the hygroscopicity as compared with PAG conventionally examined as a refrigeration lubricant for HFC-134a. Therefore, by the used the refrigeration lubricants comprising the ester according to used in the invention as a main component can solve the problems on the compatibility with HFC-134a and the hygroscopicity, which have never been solved in the conventional technique, can be solved and the electric insulating property, which comes into problem when HFC-134a is used in a compressor for a refrigerator, can be further enhanced.

Moreover, additives usually used in the lubricant such as antioxidant, anti-wear agent, epoxy compound, and the like for instance may properly be added to the refrigeration lubricant used in according to the invention.

Examples 1-6

The performances as a refrigeration lubricant using HFC-134a as a refrigerant were evaluated with respect to ~~eight~~ six esters A-1 - A-6 shown in the following Table 1 (all of which esters were not commercially available but were prepared according to the first invention). For the comparison, the same evaluation as mentioned above was made with respect to commercially available PAG (B-1 - B-3, made by Asahi Denka Co., Ltd.) and esters (C-1 - C-2, made by Nippon Oil and Fats Co., Ltd.) as a refrigeration lubricant shown in the following Table 2.

The lubricity, compatibility, thermal stability, electric insulating property and hygroscopicity as performances of the refrigeration lubricant for the compressor shown in Tables 1 and 2 were evaluated under the following conditions.

Lubricity

Seizuring load (Falex load-carrying capacity) was measured according to ASTM D-3233-73 under a controlled atmosphere of HFC-134a blown.

Compatibility

After 0.6 g of the test lubricant and 2.4 g of the refrigerant (HFC-134a) were sealed in a glass tube, the cooling at 1°C/min and the heating

were carried out, during which a temperature causing two-phase separation was measured.

Thermal stability

After 1 g of the test lubricant, 1 g of the refrigerant (HFC-134a or R-12) and a catalyst (wire of iron, copper or aluminium) were sealed in a glass tube, the mixture was heated to 175°C, and a color of the lubricant after 10 days was judged by ASTM color system according to ANSI/ASHRAE 97-1983.

Electric insulating property

It was evaluated by a dielectric constant at 80°C according to JIS C-2101.

Hygroscopicity

Into a beaker of 100 ml was charged 60 g of the test lubricant, which was left to stand at a temperature of 25°C and a humidity of 70% for 3 hours and then the water concentration was measured.

The evaluation results are shown in the following Table 3.

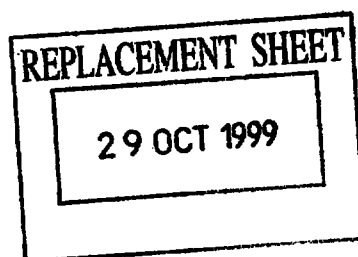


Table 1

Item Ester	Polyvalent alcohol	Polybasic acid			Dynamic viscosity at 40°C (cSt) mm ² /S	Color (ASTM)
		straight chain fatty acid (mol%)	branched-chain fatty acid (mol%)	polybasic acid (mol%)		
A-1	pentaerythritol	—	isononanoic acid (100)	—	125.4	L 0.5
A-2	pentaerythritol	—	2-ethylhexanoic acid (100)	—	42.3	L 0.5
A-3	pentaerythritol	heptanoic acid (15)	isobutanoic acid (75)	adipic acid (10)	110.9	L 0.5
A-4	dipentaerythritol	propionic acid (30)	2-ethylhexanoic acid (70)	—	123.9	L 0.5
A-5	dipentaerythritol	—	isobutanoic acid (90) isostearic acid (10)	—	68.	L 0.5
A-6	tripentaerythritol	propionic acid (20)	2-ethylhexanoic acid (80)	—	146.3	L 0.5

Note) Mol% is an amount per total acid.

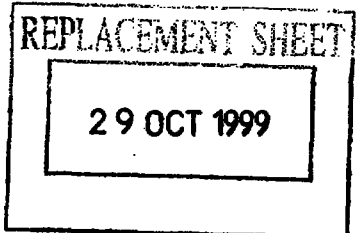


Table 2

	Type	Trade name	Color (ASTM)	Dynamic viscosity at 40°C (cSt) mm^2/s
B-1	PAG 1	Adekapol M-30 1)	L 0.5	32.8
B-2	PAG 1	Adekapol M-110 2)	L 0.5	105.2
B-3	PAG 1	Adekapol MH-50 3)	L 0.5	54.6
C-1	ester	dioctyl sebacate	L 0.5	11.4
C-2	ester	Unistar MB-816 4)	L 0.5	8.1

1) polyoxypropylene glycol monoalkyl ether

2) polyoxypropylene glycol monoalkyl ether

3) polyoxyethylene propylene glycol monoalkyl ether

4) monoester of 2-ethylhexanol and palmitic acid

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Table 3

Test lubricant used in the invention	Dielectric constant at 80°C (Ω.cm)	Two-phase separation temperature (°C)		Seizuring load (Kgf)	Thermal stability				Hygroscopicity (water content, ppm)
		low temperature	high temperature		refrigerant R-12		refrigerant HFC-134a		
					color (ASTM)	sludge	color (ASTM)	sludge	
A-1	6.5×10^{13}	-38	80≤	641	L 1.0	none	L 1.0	none	292
A-2	1.7×10^{13}	≤-50	80≤	549	L 1.0	none	L 1.0	none	331
A-3	4.1×10^{12}	-43	80≤	610	L 1.0	none	L 1.0	none	348
A-4	2.6×10^{12}	-40	80≤	623	L 1.0	none	L 1.0	none	325
A-5	1.4×10^{13}	≤-50	80≤	581	L 1.0	none	L 1.0	none	339
A-6	4.5×10^{12}	-31	80≤	654	L 1.0	none	L 1.0	none	324

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Table 3 (Continue)

Test lubricant used for comparison	Dielectric constant at 80°C ($\Omega \cdot \text{cm}$)	Two-phase separation temperature (°C)		Seizuring load (Kgf)	Thermal stability				Hygroscopicity (water content, ppm)
		low temperature	high temperature		refrigerant R-12	refrigerant HFC-134a	color (ASTM)	sludge	
B-1	2.1×10^7	≤ -50	67	430	8.0 $\leq$	many	L 1.0	none	1600
B-2	2.8×10^7	insoluble	insoluble	460	8.0 $\leq$	many	L 1.0	none	1200
B-3	$\leq 10^7$	≤ -50	53	430	8.0 $\leq$	many	L 1.0	none	2100
C-1	5.1×10^{12}	insoluble	insoluble	570	L 1.0	none	L 1.0	none	340
C-2	4.3×10^{12}	insoluble	insoluble	590	L 1.0	none	L 1.0	none	365

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As seen from Table 3, when the esters ~~according to~~ used in the invention are compared with the conventional PGA (B-1 - B-3) used for comparison shown in Tables 2 and 3, the electric insulating property represented by the dielectric constant is 100,000 times or more and the two-phase separation at a high temperature is not caused. Furthermore, the seizing load is excellent and the hygroscopicity is low. The thermal stability is equal in case of the HFC-134a system, but is considerably excellent in case of the R-12 system. This is very advantageous in practical use because the mixing of HFC-134a and R-12 is not avoided at a stage of replacing the refrigerant from R-12 to HFC-134a.

On the other hand, when the esters ~~according to~~ used in the invention are compared with the commercially available esters (C-1 - C-2) used for comparison shown in Tables 2 and 3, the two-phase separation temperature is extremely different and the conventional esters are insoluble in HFC-134a. In this point, the molecule designed esters ~~according to~~ used in the invention have a great merit.

As seen from the above, the esters ~~according to~~ used in the invention are fairly excellent in the performances as a lubricant as compared with ~~Comparative Examples~~ those used for comparison.

The HFC-134a has been mentioned as a possible replacement for R-12 and is used for car air conditioner and refrigerator, ~~and the like~~ for instance. Particularly, in case of the car air conditioner, the compressor is driven in summer season, so that the compatibility between oil and refrigerant at high temperature becomes important. When the two-phase separation between oil and refrigerant is caused in the compressor during the driving, the refrigerant having a larger specific gravity remains in the lower portion of the compressor, resulting in the occurrence of compressor seizing.

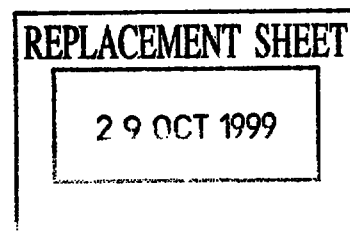
In case of the refrigerator, the motor is included in the compressor, so that leakage of electricity comes into problem. In this connection, the esters ~~according to~~ used in the invention have a dielectric constant higher by 100,000 times or more than that of the conventional PAG and are excellent in the electric insulating property, so that they can be said to be

refrigeration lubricant for the refrigerator.

5 Concretely, lubricants having a dynamic viscosity of 10-50 mm^2/s (cSt) at 40°C are used as a lubricant for the refrigerator requiring a two-phase separation temperature of not higher than -40°C, so that the esters A-2 is particularly suitable therefor. On the other hand, lubricants having a dynamic viscosity of 80-150 mm^2/s (cSt) at 40°C are used as a lubricant for the car air conditioner requiring a two-phase separation temperature of not higher than -20°C, so that the esters A-1, A-3, A-4, and A-6 are particularly
10 suitable therefor.

 Recently, HFC-134a causing substantially no breakage of ozone layer is closed up instead of R-12 widely used as a refrigerant in order to cope with the breakage of ozone layer through chlorofluorocarbon and hydrochlorofluorocarbon being a greatest problem in world-wide scale, but
15 is poor in the compatibility with the conventional refrigeration lubricant, which is a bar for the development of replacement system. However, the refrigeration lubricants ~~according to~~ used in the invention have a sufficient compatibility with HFC-134a as a refrigerant and a high electric insulating property and also are excellent in the total performances, so that they have
20 the effect that the conventional systems can be used as they are even when HFC-134a is used instead of the conventional R-12 and R-22 as a refrigerant.

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Claims

1. Use of a lubricant for compressors using a hydrofluorocarbon refrigerant containing no chlorine, comprising as a main component an ester(s) obtainable by reacting (a) at least one polyvalent alcohol selected from the group consisting of pentaerythritol, dipentaerythritol and tripentaerythritol with (b) a mixture of at least one of straight chain monovalent fatty acids having a carbon number of 3-11 with at least one of branched-chain monovalent fatty acids having a carbon number of 4-14, wherein the amount of the branched-chain monovalent fatty acid is not less than 50 mol% per total monovalent fatty acid used, ~~or branched chain monovalent saturated fatty acid having a carbon number of 2-18.~~
2. ~~The use~~ ^A Use of a lubricant according to Claim 1, wherein said straight chain monovalent fatty acid is selected from the group consisting of propionic acid, butanoic acid, pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, decanoic acid and undecanoic acid, and said branched-chain monovalent fatty acid is selected from the group consisting of isobutanoic acid, isopentanoic acid, isoheptanoic acid, 2-ethylhexanoic acid and 3,5,5-trimethylhexanoic acid.
3. ^A Use of a lubricant according to claim 1, wherein said branched-chain monovalent fatty acid is one having a carbon number of 7-9.
4. Use of a lubricant according to any one of claims 1 to 3, wherein said ester has a total acid value of not more than 3 mgKOH/g and a hydroxyl value of not more than 50 mgKOH/g.
5. ~~The use~~ ^A Use of a lubricant according any one of claims 1 to ~~6-4,~~ wherein said hydrofluorocarbon refrigerant is 1,1,1,2-tetrafluoroethane.
6. ~~A~~ ^A Use of a lubricant for compressors using a hydrofluorocarbon refrigerant containing no chlorine, comprising as a main component an ester(s) ~~obtained~~ obtainable by reacting (a) at least one polyvalent alcohol selected from the group consisting of pentaerythritol, dipentaerythritol and tripentaerythritol with (b) a mixture of at least one of straight chain monovalent fatty acids having a carbon number of 3-11 with at least one of branched-chain monovalent fatty acids having a carbon number of 4-14, wherein the amount of the



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branched-chain monovalent fatty acid is not less than 50 mol% per total monovalent fatty acid used, and (c) at least one polybasic acid having a carbon number of 4-10, wherein the amount of the polybasic acid is not more than 80 mol% per total fatty acid.

- 5 7. Use of a lubricant according to claim 6, wherein said straight chain monovalent fatty acid is selected from the group consisting of propionic acid, butanoic acid, pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, nonanoic acid, decanoic acid and undecanoic acid, and said branched-chain monovalent fatty acid is selected from the group consisting of isobutanoic acid, isopentanoic acid, isoheptanoic acid, 2-ethylhexanoic acid and 3,5,5-trimethylhexanoic acid.
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- 15 8. Use of a lubricant according to claim 6, wherein said polybasic acid is selected from the group consisting of succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid and sebacic acid.
- 20 9. Use of a lubricant according to any one of claims 6 to 8, wherein said ester has a total acid value of not more than 3 mgKOH/g and a hydroxyl value of not more than 50 mgKOH/g.
- 25 10. Use of a lubricant according to any one of claims 6 to 9, wherein said hydrofluorocarbon refrigerant is 1,1,1,2-tetrafluoroethane.
- 30 11. Use of a lubricant for compressors using a hydrofluorocarbon refrigerant containing no chlorine, said lubricant comprising as a main component (an) ester(s) obtainable by reacting (a) at least one polyvalent alcohol selected from pentaerythritol and dipentaerythritol, with (b) at least one branched-chain monovalent fatty acid selected from isobutanoic acid, isopentanoic acid, isoheptanoic acid and isononanoic acid.
12. Use of a lubricant according to claim 11, wherein said polyvalent alcohol is pentaerythritol.
13. Use of a lubricant for compressors using a hydrofluorocarbon refrigerant containing no chlorine, said lubricant comprising as a main component (an) ester(s) obtainable by reacting (a) at least one polyvalent alcohol selected from pentaerythritol and dipentaerythritol, with (b) at least one branched-chain monovalent fatty acid having a carbon number of 4 to 18,



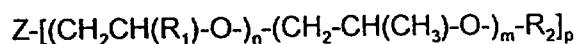
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with the proviso that

- i) said lubricant does not contain a polyether polyol in an amount of 5 to 95 weight percent according to the general formula



wherein

Z is the residue of a compound having 1 to 8 active hydrogens,

R₁ is hydrogen, ethyl or mixtures thereof

n is 0 or a positive number,

m is a positive number,

n+m is a number having a value which will give a polyether polyol with a number average molecular weight range from about 400 to about 5000,

R₂ is hydrogen or an alkyl group of 1 to 6 carbon atoms,

p is an integer having a value equal to the number of active hydrogens of Z,

and

- ii) said lubricant is not used in a liquid composition comprising a major amount (more than 50% by weight) of a fluorine containing hydrocarbon refrigerant and a minor amount of (less than 50% by weight) of said lubricant.

14. Use of a lubricant according to claim 13, wherein said polyvalent alcohol is pentaerythritol.
15. Use of a lubricant according to claim 13 or 14, wherein said branched-chain monovalent fatty acid is selected from the group consisting of isobutanoic acid, isopentanoic acid, isoheptanoic acid, 2-ethylhexanoic acid, isononanoic acid and 3,5,5-trimethylhexanoic acid.
16. Use of a lubricant according to Claim 13 or 14, wherein said branched-chain monovalent fatty acid is one having a carbon number of 7-9.



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17. Use of a lubricant according to claim 16, wherein said branched-chain monovalent fatty acid is selected from the group consisting of isoheptanoic acid, 2-ethylhexanoic acid, isononanoic acid and 3,5,5-trimethylhexanoic acid.
18. Use of a lubricant according to any one of claims 11 to 17, wherein said hydrofluorocarbon refrigerant is 1,1,1,2-tetrafluoroethane.

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