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(54) **Use of a lubricant for compressors using a hydrofluorocarbon refrigerant containing no chlorine**

Vervendung eines Schmierstoffs für Kompressoren, die ein chlorfreies  
Fluorkohlenwasserstoff-Kältemittel verwenden

Utilisation d'un lubrifiant pour des compresseurs utilisant un réfrigérant hydrofluorocarboné ne  
contenant pas de chlore

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**EP-A- 0 378 176 WO-A-90/12489**  
**US-A- 4 826 633 US-A- 4 851 144**

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- **DATABASE WPIL, accession no. 81-87972D [48],**  
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- **DATABASE WPIL, accession no. 84-267230 [43],**  
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**JP-A-59 164 393 (NIPPON OILS & FATS K.K.)**
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- **DATABASE WPIL, accession no. 81-03048D [03],**  
**Derwent Publications Ltd, London, GB; &**  
**JP-A-55 145 638 (NIPPON OILS & FATS K.K.)**

## Description

[0001] This invention relates to the use of lubricants for compressors using a hydrofluorocarbon refrigerant containing no chlorine such as hydrofluorocarbons (HFC), preferably HFC-134a, (1,1,1,2-tetrafluoroethane).

[0002] 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) have been used as a refrigerant for freezers, air conditioners and refrigerators, for instance.

[0003] JP-A-56131548 discloses neopentylpolyolesters useful as freon-resisting oil for lubrication.

[0004] 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.

[0005] 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 are proposed as a possible replacement for R-12, causing no breakage of ozone layer.

[0006] 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 saving property, anti-wear performance, sealability, thermal stability, prevention of sludge formation, for instance are mentioned as performances required in the refrigeration lubricant, so that they are required to be considered in the development of the above countermeasure.

[0007] 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.

[0008] However, the conventional synthetic lubricants as mentioned above cannot be a refrigeration lubricant using HFC-134a as a refrigerant from a viewpoint of compatibility, for instance.

[0009] 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  $-40^{\circ}\text{C}$  and  $+50^{\circ}\text{C}$ .

[0010] On the contrary, HFC-134a is a replacing refrigerant of R-12 and is mainly expected for use in a car air conditioner or refrigerator, 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 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.

[0011] It is an object of the invention to provide a refrigeration lubricant, which has excellent compatibility with a new refrigerant such as HFC-134a within a wide temperature range, a high electric insulating property and a low hygroscopicity, for compressors using a hydrofluorocarbon refrigerant containing no chlorine.

[0012] At the present, a part of commercially available esters is used in systems using refrigerants such as R-12 and R-22, 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.

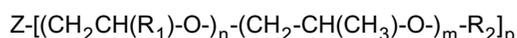
[0013] The present invention refers to the use of a lubricant for compressors using a hydrofluorocarbon refrigerant containing no chlorine, comprising as a main component an ester(s) obtainable by reacting (a) at least one polyvalent alcohol selected from the group consisting of pentaerythritol, dipentaerythritol 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, with the proviso that 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.

**[0014]** 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 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 with the proviso that 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.

**[0015]** 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,

R<sub>1</sub> 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,

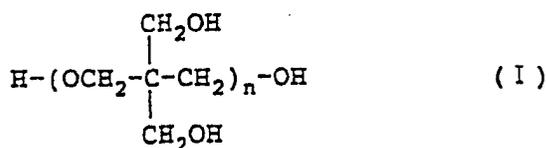
R<sub>2</sub> is hydrogen or an alkyl group of 1 to 6 carbon atoms,

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.

**[0016]** Pentaerythritol, dipentaerythritol and tripentaerythritol are represented by the following formula (I):



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

**[0017]** In a preferred embodiment of the invention, the hydrofluorocarbon refrigerant is 1,1,1,2-tetrafluoroethane (HFC-134a).

**[0018]** In the condensate of pentaerythritol, the polymerization degree may be determined in accordance with the viscosity required in the resulting synthesized ester.

**[0019]** 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.

**[0020]** At least one of branched-chain monovalent fatty acids 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-chain mono-

valent 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.

**[0021]** In order to obtain a sufficiently satisfactory compatibility with the refrigerant HFC-134a and the like, 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 4-14, preferably 7-9 as the monovalent fatty acid can be used.

**[0022]** 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.

**[0023]** 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 4-10 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 acids are used: succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, phthalic acid, maleic acid and trimellitic acid.

**[0024]** The ester compounds 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 anhydride, an acid chloride or the like as a derivative of the fatty acid.

**[0025]** 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.

**[0026]** The esters 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. 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 refrigeration lubricants comprising the ester used in the invention as a main component 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.

**[0027]** Moreover, additives usually used in the lubricant such as antioxidant, anti-wear agent, and epoxy compound, for instance may properly be added to the refrigeration lubricant used in the invention.

#### Examples 1-6

**[0028]** The performances as a refrigeration lubricant using HFC-134a as a refrigerant were evaluated with respect to 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 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.

**[0029]** 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

**[0030]** Seizing load (Falex load-carrying capacity) was measured according to ASTM D-3233-73 under a controlled atmosphere of HFC-134a blown.

#### Compatibility

**[0031]** 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

**[0032]** 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 according to ANSI/ASHRAE 97-1983.

#### Electric insulating property

**[0033]** It was evaluated by a dielectric constant at 80°C according to JIS C-2101.

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### Hygroscopicity

**[0034]** Into a beaker of 100 ml there were 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.

5 **[0035]** The evaluation results are shown in the following Table 3.

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Table 1

Item	Polyvalent alcohol	Polybasic acid			Dynamic viscosity at 40°C (cSt) mm <sup>2</sup> /S	Color (ASTM)
		straight chain fatty acid (mol%)	branched-chain fatty acid (mol%)	polybasic acid (mol%)		
Λ-1	pentaerythritol	—	isononanoic acid (100)	—	125.4	L 0.5
Λ-2	pentaerythritol	—	2-ethylhexanoic acid (100)	—	42.3	L 0.5
Λ-3	pentaerythritol	heptanoic acid (15)	isobutanoic acid (75)	adipic acid (10)	110.9	L 0.5
Λ-4	dipentaerythritol	propionic acid (30)	2-ethylhexanoic acid (70)	—	123.9	L 0.5
Λ-5	dipentaerythritol	—	isobutanoic acid (90) isostearic acid (10)	—	68.	L 0.5
Λ-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 <sup>2</sup> /J	
5	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
10	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			
A-1	$6.5 \times 10^{13}$	-38	80≤	641	color (ASTM)	sludge	refrigerant R-12	refrigerant HFC-134a	color (ASTM)	sludge	292
A-2	$1.7 \times 10^{13}$	≤-50	80≤	549	L 1.0	none	none	L 1.0	L 1.0	none	331
A-3	$4.1 \times 10^{12}$	-43	80≤	610	L 1.0	none	none	L 1.0	L 1.0	none	348
A-4	$2.6 \times 10^{12}$	-40	80≤	623	L 1.0	none	none	L 1.0	L 1.0	none	325
A-5	$1.4 \times 10^{13}$	≤-50	80≤	581	L 1.0	none	none	L 1.0	L 1.0	none	339
A-6	$4.5 \times 10^{12}$	-31	80≤	654	L 1.0	none	none	L 1.0	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 sludge (ASTM)	color sludge (ASTM)	
B-1	$2.1 \times 10^7$	≤-50	67	430	8.0 ≤	many	L 1.0	none	1600
B-2	$2.8 \times 10^7$	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	$5.1 \times 10^{12}$	insoluble	insoluble	570	L 1.0	none	L 1.0	none	340
C-2	$4.3 \times 10^{12}$	insoluble	insoluble	590	L 1.0	none	L 1.0	none	365

[0036] As seen from Table 3, when the esters 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.

[0037] On the other hand, when the esters 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 used in the invention have a great merit.

**[0038]** As seen from the above, the esters used in the invention are fairly excellent in the performances as a lubricant as compared with those used for comparison.

**[0039]** The HFC-134a has been mentioned as a possible replacement for R-12 and is used for car air conditioner and refrigerator, 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.

**[0040]** 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 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 a refrigeration lubricant for the refrigerator.

**[0041]** Concretely, lubricants having a dynamic viscosity of 10-50 mm<sup>2</sup>/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 ester A-2 is particularly suitable therefor. On the other hand, lubricants having a dynamic viscosity of 80-150 mm<sup>2</sup>/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.

**[0042]** 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 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, with the proviso that  
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.
2. 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 anyone 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. Use of a lubricant according to any one of claims 1 to 4, wherein said hydrofluorocarbon refrigerant is 1,1,1,2-tetrafluoroethane.
6. 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, 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, with the proviso that 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.

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.
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. 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 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,  
 R<sub>1</sub> 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<sub>2</sub> 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.

12. Use of a lubricant according to claim 11, wherein said polyvalent alcohol is pentaerythritol.
13. Use of a lubricant according to claim 11 or 12, wherein 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.
14. Use of a lubricant according to claim 11 or 12, wherein said branched-chain monovalent fatty acid is one having a carbon number of 7-9.
15. Use of a lubricant according to claim 14, wherein said branched-chain monovalent fatty acid is selected from the group consisting of isoheptanoic acid, 2-ethylhexanoic acid, and 3,5,5-trimethylhexanoic acid.
16. Use of a lubricant according to any one of claims 11 to 15, wherein said hydrofluorocarbon refrigerant is

1,1,1,2-tetrafluoroethane.

### Patentansprüche

- 5
1. Verwendung eines Schmiermittels für Kompressoren unter Verwendung eines Fluorkohlenwasserstoff-Kühlmittels, das kein Chlor enthält, umfassend als Hauptbestandteil (einen) Ester, erhältlich durch Umsetzen von (a) mindestens einem polyvalenten Alkohol, ausgewählt aus Pentaerythritol, Dipentaerythritol und Tripentaerythritol mit (b) einer Mischung von mindestens einer von geradkettigen monovalenten Fettsäuren mit einer Kohlenstoffanzahl von 3 - 11 mit mindestens einer von verzweigt-kettigen monovalenten Fettsäure mit einer Kohlenstoffanzahl von 4 - 14, worin die Menge der verzweigt-kettigen monovalenten Fettsäure nicht weniger als 50 mol-% pro verwendete Gesamtmenge monovalenter Fettsäure ist, mit der Massgabe, dass das Schmiermittel nicht in einer flüssigen Zusammensetzung, die als Hauptbestandteil (mehr als 50 Gew.-%) ein fluorhaltiges Kohlenwasserstoff-Kühlmittel und als Nebenbestandteil (weniger als 50 Gew.-%) das Schmiermittel enthält, verwendet wird.
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- 15
2. Verwendung eines Schmiermittels nach Anspruch 1, worin die geradkettige monovalente Fettsäure ausgewählt ist aus Propansäure; Butansäure, Pentansäure, Hexansäure, Heptansäure, Octansäure, Nonansäure, Decansäure und Undecansäure, und die verzweigt-kettige monovalente Fettsäure ausgewählt ist aus Isobutansäure, Isopentansäure, Isoheptansäure, 2-Ethylhexansäure und 3,5,5-Trimethylhexansäure.
- 20
3. Verwendung eines Schmiermittels nach Anspruch 1, worin die verzweigt-kettige monovalente Fettsäure eine mit einer Kohlenstoffanzahl von 7 - 9 ist.
- 25
4. Verwendung eines Schmiermittels nach einem der Ansprüche 1 bis 3, worin der Ester eine Gesamtsäurezahl von nicht mehr als 3 mgKOH/g und eine Hydroxylzahl von nicht mehr als 50 mgKOH/g hat.
- 30
5. Verwendung eines Schmiermittels nach einem der Ansprüche 1 bis 4, worin das Fluorkohlenwasserstoff-Kühlmittel 1,1,1,2-Tetrafluorethan ist.
- 35
6. Verwendung eines Schmiermittels für Kompressoren unter Verwendung eines Fluorkohlenwasserstoff-Kühlmittels, das kein Chlor enthält, umfassend als Hauptbestandteil (einen) Ester, erhältlich durch Umsetzen von (a) mindestens einem polyvalenten Alkohol, ausgewählt aus Pentaerythritol, Dipentaerythritol und Tripentaerythritol mit (b) einer Mischung von mindestens einer von geradkettigen monovalenten Fettsäuren mit einer Kohlenstoffanzahl von 3 - 11 mit mindestens einer von verzweigt-kettigen monovalenten Fettsäure mit einer Kohlenstoffanzahl von 4 - 14, worin die Menge der verzweigt-kettigen monovalenten Fettsäure nicht kleiner ist als 50 mol-% pro verwendeter Gesamtmenge an monovalenter Fettsäure, und (c) mindestens einer polybasischen Säure mit einer Kohlenstoffanzahl von 4 - 10, worin die Menge der polybasischen Säure nicht mehr als 80 mol-% pro Gesamtfettsäure ist, mit der Massgabe, dass das Schmiermittel nicht in einer flüssigen Zusammensetzung, die als Hauptbestandteil (mehr als 50 Gew.-%) ein fluorhaltiges Kohlenwasserstoff-Kühlmittel und als Nebenbestandteil (weniger als 50 Gew.-%) das Schmiermittel enthält, verwendet wird.
- 40
7. Verwendung eines Schmiermittels nach Anspruch 6, worin die geradkettige monovalente Fettsäure ausgewählt ist aus Propionsäure, Butansäure, Pentansäure, Hexansäure, Heptansäure, Octansäure, Nonansäure, Decansäure und Undecansäure, und die verzweigt-kettige monovalente Fettsäure ausgewählt ist aus Isobutansäure, Isopentansäure, Isoheptansäure, 2-Ethylhexansäure und 3,5,5-Trimethylhexansäure.
- 45
8. Verwendung eines Schmiermittels nach Anspruch 6, worin die polybasische Säure ausgewählt ist aus Succinsäure, Glutarsäure, Adipinsäure, Pimelinsäure, Suberinsäure, Azelainsäure und Sebacinsäure.
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9. Verwendung eines Schmiermittels nach einem der Ansprüche 6 bis 8, worin der Ester eine Gesamtsäurezahl von nicht mehr als 3 mgKOH/g und eine Hydroxylzahl von nicht mehr als 50 mgKOH/g hat.
- 55
10. Verwendung eines Schmiermittels nach einem der Ansprüche 6 bis 9, worin das Fluorkohlenwasserstoff-Kühlmittel 1,1,1,2-Tetrafluorethan ist.
11. Verwendung eines Schmiermittels für Kompressoren unter Verwendung eines Fluorkohlenwasserstoff-Kühlmittels, das kein Chlor enthält, das als Hauptkomponente (einen) Ester umfasst, erhältlich durch Umsetzen von (a) mindestens einem polyvalenten Alkohol, ausgewählt aus Pentaerythritol und Dipentaerythritol mit (b) mindestens einer

verzweigt-kettigen monovalenten Fettsäure mit einer Kohlenstoffanzahl von 4 bis 18, mit der Massgabe, dass

(i) das Schmiermittel kein Polyetherpolyol in einer Menge 5 bis 95 Gew.-% gemäss der allgemeinen Formel

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enthält, worin

Z der Rest einer Verbindung mit 1 bis 8 aktiven Wasserstoffen ist,

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R ist Wasserstoff, Ethyl oder Mischungen davon

n ist 0 oder eine positive Zahl,

m ist eine positive Zahl,

n+m ist eine Zahl mit einem Wert, welcher dem Polyetherpolyol eine mittlere

15

Molekulargewichtszahl im Bereich von ca. 400 bis ca. 5000 verleiht,

R<sub>2</sub> ist Wasserstoff oder eine Alkylgruppe mit 1 bis 6 Kohlenstoffatomen,

p ist eine ganze Zahl mit einem Wert,

entsprechend der Zahl der aktiven Wasserstoffe von Z,

und

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(ii) das Schmiermittel nicht in einer flüssigen Zusammensetzung, die als Hauptbestandteil (mehr als 50 Gew.-%) ein fluorhaltiges Kohlenwasserstoff-Kühlmittel und als Nebenbestandteil (weniger als 50 Gew.-%) das Schmiermittel enthält, verwendet wird.

25

12. Verwendung eines Schmiermittels nach Anspruch 11, worin der polyvalente Alkohol Pentaerythritol ist.

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13. Verwendung eines Schmiermittels nach Anspruch 11 oder 12, worin die verzweigt-kettige monovalente Fettsäure ausgewählt ist aus Isobutansäure, Isopentansäure, Isoheptansäure, 2-Ethylhexansäure und 3,5,5-Trimethylhexansäure.

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15. Verwendung eines Schmiermittels nach Anspruch 14, worin die verzweigt-kettige monovalente Fettsäure ausgewählt ist aus Isoheptansäure, 2-Ethylhexansäure und 3,5,5-Trimethylhexansäure.

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## Revendications

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1. Utilisation d'un lubrifiant pour des compresseurs utilisant un réfrigérant hydrofluorocarboné ne contenant pas de chlore, comprenant comme constituant principal un (des) ester(s) pouvant être obtenu(s) en faisant réagir (a) au moins un alcool polyvalent choisi dans le groupe constitué du pentaérythritol, du dipentaérythritol et du tripentaérythritol avec (b) un mélange d'au moins l'un des acides gras monovalents à chaîne linéaire ayant un nombre d'atomes de carbone de 3-11 avec au moins un des acides gras monovalents à chaîne ramifiée ayant un nombre d'atomes de carbone de 4-14, où la quantité de l'acide gras monovalent à chaîne ramifiée n'est pas inférieure à 50 moles % par acide gras monovalent total employé, à condition que le lubrifiant n'est pas utilisé dans une composition liquide contenant une quantité principale (supérieure à 50 % en poids) d'un réfrigérant hydrocarboné contenant du fluor et une quantité mineure (inférieure à 50 % en poids) dudit lubrifiant.

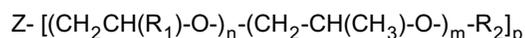
55

2. Utilisation d'un lubrifiant selon la revendication 1, dans laquelle ledit acide gras monovalent à chaîne linéaire est choisi dans le groupe constitué de l'acide propionique, de l'acide butanoïque, de l'acide pentanoïque, de l'acide hexanoïque, de l'acide heptanoïque, de l'acide octanoïque, de l'acide nonanoïque, de l'acide décanoïque et de l'acide undécanoïque, et ledit acide gras monovalent à chaîne ramifiée est choisi dans le groupe constitué de l'acide isobutanoïque, de l'acide isopentanoïque, de l'acide isoheptanoïque, de l'acide 2-éthylhexanoïque et de l'acide 3,5,5-triméthylhexanoïque.

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3. Utilisation d'un lubrifiant selon la revendication 1, dans laquelle ledit acide gras monovalent à chaîne ramifiée est un acide ayant un nombre d'atomes de carbone de 7-9.
- 5 4. Utilisation d'un lubrifiant selon l'une quelconque des revendications 1 à 3, dans laquelle ledit ester a un indice d'acide total non supérieur à 3 mg de KOH/g et un indice d'hydroxyle non supérieur à 50 mg de KOH/g.
- 10 5. Utilisation d'un lubrifiant selon l'une quelconque des revendications 1 à 4, dans laquelle ledit réfrigérant hydrofluorocarboné est le 1,1,1,2-tétrafluoroéthane.
- 15 6. Utilisation d'un lubrifiant pour des compresseurs utilisant un réfrigérant hydrofluorocarboné ne contenant pas de chlore, comprenant comme constituant principal un (des) ester(s) pouvant être obtenu(s) en faisant réagir (a) au moins un alcool polyvalent choisi dans le groupe constitué du pentaérythritol, du dipentaérythritol et du tripentaérythritol avec (b) un mélange d'au moins un des acides gras monovalents à chaîne linéaire ayant un nombre d'atomes de carbone de 3-11 avec au moins un des acides gras monovalents à chaîne ramifiée ayant un nombre d'atomes de carbone de 4-14, où la quantité de l'acide gras monovalent à chaîne ramifiée n'est pas inférieure à 50 moles % par acide gras monovalent total employé, et (c) au moins un acide polybasique ayant un nombre d'atomes de carbone de 4-10, où la quantité de l'acide polybasique n'est pas supérieure à 80 moles % par acide gras total, à condition que le lubrifiant n'est pas utilisé dans une composition liquide contenant une quantité principale (supérieure à 50 % en poids) d'un réfrigérant hydrocarboné contenant du fluor et une quantité mineure (inférieure à 50 % en poids) dudit lubrifiant.
- 20 7. Utilisation d'un lubrifiant selon la revendication 6, dans laquelle ledit acide gras monovalent à chaîne linéaire est choisi dans le groupe constitué de l'acide propionique, de l'acide butanoïque, de l'acide pentanoïque, de l'acide hexanoïque, de l'acide heptanoïque, de l'acide octanoïque, de l'acide nonanoïque, de l'acide décanoïque et de l'acide undécanoïque, et ledit acide gras monovalent à chaîne ramifiée est choisi dans le groupe constitué de l'acide isobutanoïque, de l'acide isopentanoïque, de l'acide isoheptanoïque, de l'acide 2-éthylhexanoïque et de l'acide 3,5,5-triméthylhexanoïque.
- 25 8. Utilisation d'un lubrifiant selon la revendication 6, dans laquelle ledit acide polybasique est choisi dans le groupe constitué de l'acide succinique, de l'acide glutarique, de l'acide adipique, de l'acide pimélique, de l'acide subérique, de l'acide azélaïque et de l'acide sébacique.
- 30 9. Utilisation d'un lubrifiant selon l'une quelconque des revendications 6 à 8, dans laquelle ledit ester a un indice d'acide total non supérieur à 3 mg de KOH/g et un indice d'hydroxyle non supérieur à 50 mg de KOH/g.
- 35 10. Utilisation d'un lubrifiant selon l'une quelconque des revendications 6 à 9, dans laquelle ledit réfrigérant hydrofluorocarboné est le 1,1,1,2-tétrafluoroéthane.
- 40 11. Utilisation d'un lubrifiant pour des compresseurs employant un réfrigérant hydrofluorocarboné ne contenant pas de chlore, ledit lubrifiant comprenant comme constituant principal un (des) ester(s) pouvant être obtenus) en faisant réagir (a) au moins un alcool polyvalent choisi parmi le pentaérythritol et le dipentaérythritol, avec (b) au moins un acide gras monovalent à chaîne ramifiée ayant un nombre d'atomes de carbone de 4 à 18, à condition que :

45 i) ledit lubrifiant ne contienne pas de polyol de polyéther selon la formule générale :



50 dans laquelle  
Z est le résidu d'un composé ayant 1 à 8 atomes d'hydrogène actifs,  
R<sub>1</sub> est un atome d'hydrogène, un groupe éthyle ou des mélanges de ceux-ci,  
n est égal à 0 ou à un nombre positif,  
m est un nombre positif,  
n+m est un nombre ayant une valeur qui donnera un polyol de polyéther avec une gamme de la masse  
55 moléculaire moyenne en nombre comprise entre environ 400 et environ 5000,  
R<sub>2</sub> est un atome d'hydrogène ou un groupe alkyle ayant 1 à 6 atomes de carbone,  
p est un nombre entier ayant une valeur égale au nombre d'atomes d'hydrogène actifs de Z,  
et

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ii) ledit lubrifiant n'est pas utilisé dans une composition liquide contenant une quantité principale (supérieure à 50 % en poids) d'un réfrigérant hydrocarboné contenant du fluor et une quantité mineure (inférieure à 50 % en poids) dudit lubrifiant.

- 5     **12.** Utilisation d'un lubrifiant selon la revendication 11, dans laquelle ledit alcool polyvalent est le pentaérythritol.
- 10    **13.** Utilisation d'un lubrifiant selon la revendication 11 ou 12, dans laquelle ledit acide gras monovalent à chaîne ramifiée est choisi dans le groupe constitué de l'acide isobutanoïque, de l'acide isopentanoïque, de l'acide isoheptanoïque, de l'acide 2-éthylhexanoïque et de l'acide 3, 5, 5-triméthylhexanoïque.
- 15    **14.** Utilisation d'un lubrifiant selon la revendication 11 ou 12, dans laquelle ledit acide gras monovalent à chaîne ramifiée est un acide ayant un nombre d'atomes de carbone de 7-9.
- 20    **15.** Utilisation d'un lubrifiant selon la revendication 14, dans laquelle ledit acide gras monovalent à chaîne ramifiée est choisi dans le groupe constitué de l'acide isoheptanoïque, de l'acide 2-éthylhexanoïque, et de l'acide 3,5,5-triméthylhexanoïque.
- 25    **16.** Utilisation d'un lubrifiant selon l'une quelconque des revendications 11 à 15, dans laquelle ledit réfrigérant hydrofluorocarboné est le 1,1,1,2-tétrafluoroéthane.