

Description

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

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

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 can not be a refrigeration lubricant using HFC-134a as a refrigerant from a viewpoint of 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 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 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 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 excellent, compatibility with a new refrigerant containing no chlorine, such as HFC-134a, for instance within a wide temperature range, a high 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, for instance, 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) obtained by reacting (a) neopentyl glycol with (b) at least one branched-chain monovalent fatty acid having a carbon number of 4-18, wherein said ester has a total acid value of not more than 3 mg KOH/g and a hydroxyl value of not more than 50 mg KOH/g.

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

The refrigeration lubricant for refrigerant HFC-134a and the like comprises an ester obtained by esterifying neopentyl glycol with at least one branched-chain monovalent fatty acid having a carbon number of 4-18 wherein said ester has a total acid value of not more than 3 mg KOH/g and a hydroxyl value of not more than 50 mg KOH/g, as a main component.

The reason why the carbon number of the monovalent fatty acid is limited to 4-18 is due to the fact that when the carbon number exceeds 18, the resulting ester becomes cloudy or becomes very poor in the compatibility with the

refrigerant HFC-134a and the like.

As the monovalent fatty acid, mention may be made of isobutanoic acid, isopentanoic acid, isheptanoic acid, 2-ethyl hexanoic acid, 3,5,5-trimethyl hexanoic acid, and isostearic acid, for instance.

At least one of these monovalent fatty acids is properly mixed and esterified 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 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 4-14, 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.

According to the invention, 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 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 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, and trimellitic acid, for instance. Moreover, 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. 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 desirable physical properties.

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.

Since the ester according to the invention can be obtained by the above method, the remaining acid value and hydroxyl value are not particularly critical. However, when the acid value exceeds 3, there may be 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 not more than 3 mg KOH/g. Furthermore, when the hydroxyl value exceeds 50, there may be caused an unfavorable phenomenon that the resulting ester becomes cloudy, so that the hydroxyl value is preferable not more than 50 mg KOH/g.

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, the refrigeration lubricants comprising the ester 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, and can further enhance the electric insulating property, which comes into problem when HFC-134a is used in a compressor for a refrigerator.

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.

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 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 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 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

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	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	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 used in 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 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 used in 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 used in the invention have a great merit.

As seen from the above, the esters used in 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 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 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 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.

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 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.

Claims

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) neopentyl glycol with (b) at least one branched-chain monovalent fatty acid having a carbon number of 4-18, wherein said ester has a total acid value of not more than 3 mg KOH/g and a hydroxyl value of not more than 50 mg KOH/g.
2. Use of a lubricant according to claim 1, wherein said branched-chain monovalent fatty acid is at least one selected from the group consisting of isobutanoic acid, isopentanoic acid, isoheptanoic acid, 2-ethylhexanoic acid, 3,5,5-trimethylhexanoic acid and isostearic acid.
3. Use of a lubricant according to claim 1, wherein said hydrofluorocarbon refrigerant is 1,1,1,2-tetrafluoroethane.

Patentansprüche

1. Verwendung eines Schmiermittels für Kompressoren, bei denen ein Fluorkohlenwasserstoff-Kühlmittel, das kein Chlor enthält, verwendet wird, umfassend als Hauptkomponente einen oder mehrere Ester, erhalten durch Umsetzen von (a) Neopentylglykol mit (b) wenigstens einer verzweigt-kettigen einwertigen Fettsäure mit einer Kohlenstoffanzahl von 4 bis 18, wobei der Ester eine Gesamtsäurezahl von nicht mehr als 3 mg/KOH/g und eine Hydroxylzahl von nicht mehr als 50 mg KOH/g hat.
2. Verwendung gemäß Anspruch 1, wobei die verzweigt-kettige einwertige Fettsäure wenigstens eine ist, ausgewählt aus der Gruppe bestehend aus Isobutansäure, Isopentansäure, Isoheptansäure, 2-Ethylhexansäure, 3,5,5-Trimethylhexansäure und Isostearinsäure.
3. Verwendung eines Schmiermittels, gemäß Anspruch 1, wobei das Fluorkohlenwasserstoff-Kühlmittel 1,1,1,2-Tetrafluorethan ist.



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.

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2. Verwendung gemäß Anspruch 1, wobei die verzweigt-kettige einwertige Fettsäure wenigstens eine ist, ausgewählt aus der Gruppe bestehend aus Isobutansäure, Isopentansäure, Isoheptansäure, 2-Ethylhexansäure, 3,5,5-Trimethylhexansäure und Isostearinsäure.
3. Verwendung eines Schmiermittels, gemäß Anspruch 1, wobei das Fluorkohlenwasserstoff-Kühlmittel 1,1,1,2-Tetrafluorethan ist.

**Revendications**

1. Utilisation d'un lubrifiant pour compresseurs utilisant un réfrigérant hydrofluorocarboné ne contenant pas de chlore comprenant comme composant principal un ester ou des esters obtenus par la mise en réaction (a) de néopentyl glycol avec (b) au moins un acide gras monovalent à chaîne ramifiée ayant un nombre de carbone de 4 à 18, dans lequel ledit ester présente un indice d'acidité total qui n'est pas supérieur à 3 mg KOH/g et un indice hydroxyle qui n'est pas supérieur à 50 mg KOH/g.
2. Utilisation d'un lubrifiant selon la revendication 1, dans lequel ledit acide gras monovalent à chaîne ramifiée est au moins un acide sélectionné dans le groupe qui est constitué de l'acide isobutanoïque, de l'acide isopentanoïque, de l'acide isoheptanoïque, de l'acide 2-éthylhexanoïque, de l'acide 3,5,5-triméthylhexanoïque et de l'acide isostéarique.
3. Utilisation d'un lubrifiant selon la revendication 1, dans lequel ledit réfrigérant hydrofluorocarboné est 1,1,1,2-tétrafluoroéthane