

DESCRIPTION

LUBRICANT FOR COMPRESSION TYPE REFRIGERATION SYSTEM USING HYDROCARBON REFRIGERANT

Technical Field

The present invention relates to a lubricant for a compression type refrigeration system in which a hydrocarbon refrigerant is used, which does not have the fear of ozone layer depletion, and which comprises a lower hydrocarbon having global warming ability that is much lower than that of a halogen-containing hydrocarbon refrigerant. Further, the present invention relates to a working fluid composition comprising the hydrocarbon refrigerant and the lubricant, and to a refrigeration system which is filled with the working fluid composition.

Background of the Invention

A compression type refrigeration system is constructed by a compressor, a condenser, an expansion mechanism (such as an expansion valve), an evaporator and others, and conducts refrigeration by utilizing such a property that when a refrigerant with high volatility evaporates, the refrigerant robs evaporation heat from the circumference. The compression type refrigeration system is used in a refrigerator, a freezer, an air conditioner, a showcase, a

vending machine of beverages or ice creams, and the like. In the case of air conditioner, vending machine, and the like, by utilizing heat generated upon condensing, room heating or heating and maintaining of the beverages or foods is carried out.

Conventionally, chlorine-containing chlorofluorocarbons or hydrochlorofluorocarbons (CFC or HCFC) such as trichlorofluoromethane (R11), dichlorodifluoromethane (R12) or chlorodifluoromethane (R22) have been used as the refrigerants. However, since those CFC and HCFC cause an environmental problem in that the ozone layer depletion occurs, the productions and uses thereof are internationally restricted. At present, they are replaced into non-chlorine type hydrofluorocarbons (HFC) such as difluoromethane (R32), tetrafluoroethane (R134 or R134a) or difluoroethane (R152 or R152a), each containing no chlorine. However, although those HFC do not cause the ozone layer depletion, they have high global warming ability. As a result, it is feared that those refrigerants include problems in view of a long-term standpoint of an earth environmental protection.

Therefore, from the facts that lower hydrocarbons having a low molecular weight of about 1 to 5 carbon atoms, ammonia or the like do not cause the ozone layer depletion, and have much lower global warming ability as compared with the above-mentioned chlorine type or non-chlorine type fluorinated hydrocarbons, those are noted as an environment-friendly refrigerant. Those compounds were

conventionally not leading refrigerant, but have the actual results that they have been used from old. Further, according to JP-A-10-130685, naphthene type or paraffin type mineral oils, and synthetic oils such as alkylbenzene oil, ether oil, ester oil or fluorine oil are exemplified as the lubricants for refrigerants including the above-mentioned hydrocarbons. Of those lubricants, synthetic oils are generally expensive. Therefore, mineral oils, which are inexpensive and are easily available, are expected from the standpoint practical use.

However, there are various problems even in the combination of low molecular weight hydrocarbon refrigerants (lower hydrocarbon refrigerants) and mineral oil type lubricants. In particular, it is desired for lubricants for refrigeration system using hydrocarbon refrigerants to have excellent lubricity from the reasons described below.

Low molecular weight hydrocarbons as the refrigerant and mineral oils as the lubricant have compatibility. However, if those gravity difference is large, there may be the case where it is difficult for them to be mixed by only spontaneous diffusion. In a refrigeration system, it frequently happens that those are placed in the state being difficult to be mixed each other. For example, in case of filling a refrigerant in a compressor, there becomes a state that a refrigerant with relatively low density is deposited on a lubricant with high density, which is already filled. Further,

this state also occurs when the refrigerant returns into a compressor in the state of liquid during stop of the compressor, i.e., in the case of a so-called flooding. If the compressor is started at such a state, the lubricant gathers outside of rotation by a centrifugal force, and the lubricant does not sufficiently reach to a sliding portion such as an inner bearing that requires lubrication. As a result, there is a problem that abrasion occurs at a sliding portion, or seizure easily occurs. For this reason, as a lubricant for a refrigeration system using a low molecular weight hydrocarbon refrigerant, a lubricant with excellent lubricating properties is required and eagerly desired. Further, a chlorine type fluorinated hydrocarbon refrigerant may be expected an extreme pressure effect due to chlorine present in the molecular. However, a hydrocarbon refrigerant itself has a low molecular weight, and therefore a lubricating performance is not expected at all. This also promotes to require excellent lubricating properties for a lubricant for a refrigeration system using a hydrocarbon refrigerant.

Further, the lubricants for a refrigeration system are exposed to a refrigeration cycle where high temperature and low temperature always repeat, even though they are generally used in a closed system. For this reason, a lubricant having good stability and durability is desired.

Disclosure of the Invention

The present invention has been made to solve the above-mentioned problem, and an object of the present invention is to provide lubricants for a refrigeration system using a low molecular weight hydrocarbon refrigerant, the lubricant having excellent compatibility with the hydrocarbon refrigerant, excellent lubricating properties and stability.

The inventors of the present invention proceeded extensive investigations and discussions on mineral oil type lubricants having good compatibility with a hydrocarbon refrigerant, and have found that lubricants comprising as a main components a mineral oil having specific physical properties and the composition has excellent compatibility with a hydrocarbon refrigerant and is excellent in stability and lubricating properties in the presence of a hydrocarbon refrigerant, and have completed the present invention.

That is, the present invention is a lubricant for a refrigeration system using a hydrocarbon refrigerant, wherein the lubricant comprises as a main component a mineral oil having a kinematic viscosity at 40°C of 5-150 mm²/s (cSt), a pour point of -25°C or lower, a viscosity index of 50 or higher, %C_P and %C_A by n-d-M ring analysis of 50 or more and 12 or less, respectively, a nitrogen content of 20 ppm or lower, a sulfur content of 0.02-0.3% and an iodine value of 10 gI₂/100 g or lower.

Further, the present invention is a working fluid composition

for a compression type refrigeration system, comprising at least one kind of hydrocarbon refrigerants comprising hydrocarbon compounds having 1-5 carbon atoms, and the above-mentioned lubricant, and also a refrigeration system filling the working fluid composition.

Further, as the above-mentioned lubricant, ones further containing extreme pressure agents comprising phosphate, and/or phenol type or amine type antioxidants are preferable.

The lubricant comprising as a main component such a mineral oil has excellent compatibility with the hydrocarbon refrigerant, has high abrasion resistance regarding to a compressor sliding member, and further shows excellent stability.

Best Modes for carrying out the Invention

The mineral oil used in the lubricant of the present invention has a kinematic viscosity at 40°C of 3-150 mm²/s. If the kinematic viscosity is low, sealing property and lubricity decrease in a compressor, whereas if it becomes high, a pour point is too high, or energy efficiency lowers. Preferably, it is 5-100 mm²/s.

Further, the mineral oil has a pour point of -25°C or lower. If the pour point is too high, the fluidity of the lubricant discharged from a compressor together with a refrigerant decreases in an expansion mechanism or an evaporator, and the lubricant deposits at a low temperature part of refrigeration system. This may result

in decrease of heat transfer efficiency or causing abrasion or seizure of bearing due to shortage of lubricant in the compressor.

Further, the mineral oil has a viscosity index of 50 or more. In a refrigeration cycle, the lubricant has high temperature at discharge of a compressor, and is then exposed to low temperature at an outlet of an expansion mechanism. Thus, the lubricant is used in relatively wide temperature range. Therefore, a lubricant having high viscosity index that is small in viscosity change depending to temperature, i.e., a mineral oil having high viscosity index, is desired. In general, a lubricant containing a large amount of long-chain hydrocarbons has high viscosity index, resulting in increasing lubricating performance. Viscosity index of the mineral oil is more preferably 80 or more.

Further, the mineral oil has $\%C_p$ and $\%C_A$ by n-d-M ring analysis of 50 or more and 12 or less, respectively. The lubricity of the lubricant increase as the amount of chain hydrocarbons in the lubricant increases, in other words, as a mineral oil having larger $\%C_p$ value is used. Therefore, sufficient lubricity can be maintained even if the lubricant is diluted with low molecular weight hydrocarbon refrigerants having poor lubricating properties, and abrasion or seizure of bearing is difficult to occur. $\%C_p$ is preferably 80 or more. Further, the value of $\%C_A$ greatly affects the viscosity index, and if it is large, the viscosity index decreases, which is not preferable. $\%C_A$ is preferably 10 or less. $\%C_p$ and $\%C_A$ can be determined

by n-d-M ring analytical method defined in ASTM D3238.

Further, nitrogen content and sulfur content contained in mineral oil influence characteristics of the lubricant. If the nitrogen content exceeds 20 ppm by weight, color stability deteriorates. Therefore, the nitrogen content is 20 ppm by weight or less. Further, the sulfur content is 0.02-0.3% by weight, preferably 0.02-0.1% by weight. If the sulfur content is large, corrosion property increases, and if it is small, its lubricity decreases. Therefore, it is important to keep the sulfur content in the above-mentioned range.

Further, iodine value of the mineral oil used in the lubricant for refrigeration system of the present invention is 10 gI₂/100 g or less in order to secure stability to deterioration. If the iodine value exceeds 10 gI₂/100 g, stability deteriorates.

The hydrocarbon refrigerant used with the lubricant of the present invention is low molecular weight hydrocarbon compounds having 1-5 carbon atoms. Specific examples thereof include alkane compounds such as methane, ethane, propane, n-butane, i-butane, n-pentane, i-pentane or neopentane, and cycloparaffin compounds such as cyclopropane, cyclobutane or cyclopentane. Further, derivatives of the above-mentioned compounds in which a part of carbon bonds is a double bond (olefins corresponding to the above-mentioned compounds) can also be used. As the hydrocarbon refrigerant, those compounds can be used alone or as mixtures

appropriately mixing two kinds or more.

The effect of the present invention is exhibited by using the mineral oil having above-mentioned physical properties to the compression type refrigeration system using low molecular weight hydrocarbon refrigerant. That is, the above-mentioned mineral oil shows the above-mentioned good lubricating property and stability in the presence of hydrocarbon refrigerant, and also shows good compatibility because the mineral oil has a molecular structure far similar to that of the hydrocarbon refrigerant as compared with ester oils or ether oils. Further, the mineral oil is inexpensive as compared with ester oils or ether oils, and therefore is very useful in practical aspect.

The lubricant of the present invention may optionally contain other components, if necessary. For example, conventional lubricant base oils for refrigeration system such as mineral oils other than the above-mentioned mineral oils used in the present invention (e.g., naphthene type mineral oils), or synthetic oils (e.g., alkylbenzene oils, ether oils, ester oils or fluorinated oils) and conventional additives may appropriately be compounded. Examples of the additives include phenol type or amine type antioxidants such as 2,6-di-tertiary-butylphenol, 2,6-di-tertiary-butyl-p-cresol, 4,4-methylene-bis-(2,6-di-tertiary-butyl-p-cresol) or p,p'-di-octyl-di-phenylamine, stabilizers such as phenyl glycidyl

ether or alkyl glycidyl ether, extreme pressure agents such as tricresyl phosphate or triphenyl phosphate, oiliness agents such as glycerinmonooleate, glycerinmonooleylether or glycerinmonolauryl ether, metal inactivators such as benzotriazole, and defoamers such as polydimethyl siloxane or polymethacryl acrylate. Other than the above, conventional additives such as dispersants, viscosity index improvers, rust inhibitors, corrosion inhibitors or pour point depressants can also optionally be compounded. Those additives may be mixed with the lubricant of the present invention in an amount of generally about 10 ppm to 10% by weight. In particular, when phenol type or amine type antioxidant is added in an amount of about 0.01-0.5% by weight, stability and durability of the lubricant are greatly improved. Further, phosphates such as tricresyl phosphate or triphenyl phosphate are useful as an extreme pressure agent, and its addition in very small amount (e.g., 0.05-1.0% by weight) effectively improves lubricating properties such as seizure load or abrasion resistance.

Examples

The present invention is described in more detail as described below by referring to examples, but the invention is not limited to the specific examples.

Oils used for evaluation

To evaluate the lubricant for a refrigeration system of the present invention, mineral oils 1-8 and hard type alkyl benzenes

(HAB) 1-2, having physical properties and compositions shown in Table 1 and 2, respectively, were prepared, and used in evaluation tests described after. Of those, mineral oils 1-3 and 6 correspond to a base oil of the lubricant of the present invention.

Table 1

	Mineral oil							
	1	2	3	4	5	6	7	8
Color (ASTM)	LC.5	L0.5	L0.5	L0.5	L1.0	L0.5	L0.5	L0.5
Kinematic viscosity (mm ² /s)	21.95	14.83	9.89	13.69	27.15	27.1	26.5	25.5
Viscosity index	102	96	84	33	101	101	103	102
%C _P	63	61	59	43	66	66	68	67
%C _A	9	10	10	14	5.1	5.1	4.8	4.7
Pour point (°C)	-27.5	-27.5	-27.5	-45.0	-27.5	-27.5	-30	-30
Nitrogen content (wtppm)	11	8	7	<1	28	3	10	5
Sulfur content (wt%)	0.15	0.12	0.08	0.04	0.2	0.2	0.33	0.2
Total acid value (mgKOH/g)	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Iodine value (gI ₂ /100 g)	7.6	4.8	2.2	4.5	7.5	7.5	6.8	11.2

"<XX" means less than XX.

Table 2

	HAB	
	1	2
Color (ASTM)	L0.5	L0.5
Kinematic viscosity (mm ² /s)	14.97	9.99
Viscosity index	-14	5
%C _P	-	-
%C _A	-	-
Pour point (°C)	<-50.0	<-50.0
Nitrogen content (wtppm)	<1	<1
Sulfur content (wt%)	<0.01	<0.01
Total acid value (mgKOH/g)	0.01	0.01
Iodine value (gI ₂ /100 g)	-	-

"<XX" means less than XX.

Performance evaluation test

Base oils of mineral oils 1-4 and HAB 1-2 were used as a lubricant, i-butane (R600a) was used as a refrigerant, and performance evaluation tests such as practical performance, lubricating property (Falex seizure load) and compatibility with refrigerant were conducted.

The performance evaluation test of practical performance of lubricant was conducted by durability test by using refrigeration cycle containing a compressor for refrigerator. That is, 200 g of each lubricant comprising the above-mentioned base oil and 15 g of R600a refrigerant were charged in the compressor, and operation was conducted for 1000 hours while maintaining compressor delivery pressure of 12 kgf/cm² and a compressor surface temperature of 80°C. After completion of the durability test, the compressor was opened. The lubricant after test, i.e., used oil, was sampled, and color and total acid value were measured. Further, the compressor was disassembled, and abrasion amount of piston, cylinder, connecting rod and bearing were measured. Further, Falex seizure load and compatibility with refrigerant (two layers separation temperature) was also evaluated as lubricating property. Those measurement results are shown in Table 3.

Table 3

		Mineral oil				HAB	
		1	2	3	4	1	2
Properties of used oil	Color (ASTM)	L1.5	L1.5	L1.5	L2.0	L1.5	L1.5
	Total acid value mgKOH/g	0.01	0.01	0.01	0.04	0.03	0.03
Abrasion amount of compressor member (μm)	Piston (iron)	<1.0	<1.0	<1.0	2.1	2.5	2.9
	Cylinder (iron)	<1.0	<1.0	<1.0	<1.0	<1.0	1.3
	Connecting rod (aluminum alloy)	<1.0	<1.0	<1.0	4.2	4.9	5.6
	Bearing (iron)	<1.0	<1.0	<1.0	1.2	1.7	2.6
Falex seizure load (Lbf)		440	430	400	300	280	250
Two layers separation temperature °C (refrigerant R600a)		<-40	<-40	<-40	<-40	<-40	<-40

"<XX" means less than XX.

According to Table 3, the lubricants of the present invention (mineral oils 1-3) showed that color was low as L1.0, total acid value was 0.01 mgKOH/g that was unchanged from the value of new oil, and abrasion amount of members (piston, cylinder, connecting rod and bearing) of compressor was all 1.0 μm or less. Contrary to this, mineral oil 4 and HAB 1-2, corresponding to comparative examples had almost all values being larger than those of the above examples, and deterioration of lubricant and abrasion of compressor members were observed.

Stability test (bomb test)

With respect to mineral oils 1-8, stability test (bomb test) was conducted as follows. With respect to each of mineral oils 1-8, 100 g of the mineral oil and 20 g of isobutane (R600a refrigerant)

were filled in a 300 ml bomb. Wires (1.6 mm ϕ x 20 cm) of iron (Fe), copper (Cu) and aluminum (Al) as catalysts were further placed in the bomb. The bomb was sealed and aged at 175°C for 30 days. After aging, mineral oils 1-8 and catalysts were exampled from the bomb, and color of the mineral oils after deterioration, degree of sludge formation and change of each catalyst surface were visually observed. Discoloration degree of catalyst was evaluated with 4 grades of "large", "medium", "small" and "none". Degree of sludge formation was evaluated with 4 grades of "much", "medium", "less" and "none". The results are shown in Table 4.

Table 4

		Mineral oil							
		1	2	3	4	5	6	7	8
Color (ASTM)		L1.5	L1.5	L1.5	L2.0	L4.5	L1.5	L3.0	L3.0
Discoloration of catalyst	Fe	None	None	None	Small	Medium	None	Small	Small
	Cu	None	None	None	Small	Medium	None	Medium	Small
	Al	None	None	None	None	None	None	None	None
Sludge formation		None	None	None	None	Much	None	None	Less

According to Table 4, the lubricants of the present invention (Mineral oils 1-3 and 6) showed satisfactory stability in all items, but the lubricants that do not satisfy any one or a plurality of values specified in this invention regarding viscosity index, %C_P, nitrogen content, sulfur content % and iodine value (mineral oils 4-5 and 7-8) showed that color was poor as L2.0 or more, and discoloration of catalyst and precipitation of sludge were observed.

Evaluation of additive addition effect

To evaluate addition effect of additives, tricresyl phosphate (TCP) as an extreme pressure agent and 2,6-di-tertiary butyl-p-cresol (DBPC) as an antioxidant were added to mineral oil 1 in proportions shown in Table 5 to prepare Test oils 1-3. The same stability test (bomb test) as mentioned above was conducted, and Falex seizure load was measured. The results are shown in Table 5.

Table 5

			Test oils		
			1	2	3
Additive and its amount added (wt%)	Antioxidant (DBPC)		0.5	-	0.5
	Extreme pressure agent (TCP)		-	0.1	0.1
Bomb test	Color (ASTM)		L1.5	L1.5	L1.5
	Discoloration of catalyst	Fe	None	None	None
		Cu	None	None	None
		Al	None	None	None
	Sludge formation		None	None	None

Mineral oil 1 was used as a base oil.

Various measurement test methods regarding the above-mentioned base oils, used oils and compressor members were conducted according to the following methods. Color(ASTM) was determined by JIS K2580, kinematic viscosity and viscosity index were determined according to JIS K2283, %C_P and %C_A were determined according to n-d-M ring analyst defined in ASTM D3238, pour point

was determined by JIS K2609, sulfur content was determined according to JIS K2269, total acid value was determined according to JIS K2501, nitrogen content was determined according to JIS K2541, Falex seizure load was determined according to ASTM D3233, and compatibility with refrigerant (two layers separation temperature) was determined according to JIS K2211 (Appendix 3, provided that R600a was read in place of R12).

The lubricant for a refrigeration system of the present invention is a lubricant comprising as a main component a mineral oil having specific physical properties and composition, so that it is excellent in compatibility with hydrocarbon refrigerants and also excellent in stability and lubricating properties under the presence of hydrocarbon refrigerants. Therefore, it is very useful as a lubricant for a refrigeration system using friendly hydrocarbon refrigerant to earth environment.



CLAIMS

1. A lubricant for a compression type refrigeration system using a hydrocarbon refrigerant, characterized in that the lubricant comprises as a main component a mineral oil having a kinematic viscosity at 40°C of 3-150 mm²/s, a pour point of -25°C or lower, a viscosity index of 50 or higher, %C_P and %C_A by n-d-M ring analysis of 50 or more and 12 or less, respectively, a nitrogen content of 20 ppm or lower, a sulfur content of 0.02-0.3% and an iodine value of 10 gI₂/100g or lower.

2. The lubricant as according to claimed in claim 1, wherein the lubricant further comprises an extreme pressure agent containing a phosphate, and/or a phenol type or amine type antioxidant.

3. A working fluid composition for use in a compression type refrigeration system, characterized by comprising at least one kind of hydrocarbon refrigerants comprising hydrocarbon compounds having 1-5 carbon atoms, and a lubricant comprising as a main component a mineral oil having a kinematic viscosity at 40°C of 5-150 mm²/s, a pour point of -25°C or lower, a viscosity index of 50 or higher, %C_P and %C_A by n-d-M ring analysis of 50 or more and 12 or less, respectively, a nitrogen content of 20 ppm or lower, a sulfur content of 0.02-0.3% and an iodine value of 10 gI₂/100g or lower.

4. A refrigeration system comprising a compressor, a condenser, a dryer, an expansion mechanism and an evaporator, wherein



the refrigeration system is filled with a working fluid composition comprising at least one kind of hydrocarbon refrigerants comprising hydrocarbon compounds having 1-5 carbon atoms, and a lubricant comprising as a main component a mineral oil having a kinematic viscosity at 40°C of 5-150 mm²/s, a pour point of -25°C or lower, a viscosity index of 50 or higher, %C_P and %C_A by n-d-M ring analysis of 50 or more and 12 or less, respectively, a nitrogen content of 20 ppm or lower, a sulfur content of 0.02-0.3% and an iodine value of 10 gI₂/100g or lower.