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REFRIGERATION LUBRICATING OIL

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ABSTRACT OF THE DISCLOSURE

Lubricating oil for refrigeration equipment based on the combination of alkylbenzenes containing from 10 to 25 carbon atoms in the alkyl groups and from about 2 to about 50% by weight of polyisobutylene having a viscosity in the range of about 3000 to about 1,000,000 SUS at 100° F.

BACKGROUND OF THE INVENTION

This invention relates to lubricating oils for use in refrigeration apparatus and more particularly for use in refrigeration apparatus of either the centrifugal compressor type in which the compressor driver is outside the compressor housing or the hermetic unit type in which the motor-compressor unit is an integral assembly sealed into a gas-tight housing.

Refrigeration lubricants for use in hermetic unit designs are usually sealed in the motor-compressor unit housing and are not replaceable. They are thus required to perform under relatively severe conditions of temperature change for the life of the refrigeration unit, which is generally a period of several years of intermittent daily service. The lubricant is in contact with the refrigerant and in addition to lubricating the compressor, it serves as a seal between the low-pressure and high-pressure sides of the system. As the refrigerant flows from the compressor through the condenser and evaporator and back to the intake side of the compressor, it carries some of the lubricant with it. Thus, while the lubricant is required only at the compressor, it circulates throughout the system. In addition, the lubricant for the centrifugal compressor unit design, although replaceable, must be stable toward oxidation which commonly occurs due to air leakage around the drive shaft in order to avoid need for frequent oil changes.

The service of lubricating a refrigerator compressor and motor subjects the lubricant or oil to conditions not encountered in other types of service. These special unique conditions include: (1) rapid swings in temperature from about −100° F. to +400° F.; (2) contact with refrigerants, generally fluorinated, chlorinated methanes of the Freon types; (3) ability to serve as a pressure seal in the compressor; and (4) contact with electric motor windings. Because of these unusual conditions important properties of the oil are viscosity, viscosity index, mutual solubility with refrigerants, pour point, volatility, wear characteristics, high temperature stability, resistance to chemical reaction with refrigerants, and corrosivity to metals.

The viscosity of the oil-refrigerant mixture is a factor in determining the effectiveness of the seal between the high-pressure and low-pressure sides of the system; and because of the wide variation in temperatures throughout

the system, the viscosity index of the oil is important. An oil should be chosen with a viscosity as low as is possible, consistent with effective sealing with the refrigerant used for the entire range of temperatures and pressures encountered. Various viscosity grades of refrigerator lubricants are supplied to provide optimum service for different types of refrigeration equipment and refrigerants. The viscosity index should be high because of the very large changes in temperature encountered by the oil.

The oil and refrigerant may be completely miscible at all temperatures and pressures encountered in the refrigeration cycle, or they may separate into two phases at certain pressures and temperatures encountered. One of the phases will be rich in refrigerant and of low viscosity, while the other is rich in oil and higher in viscosity. Under conditions of higher temperature in the cycle, the mutual solubility increases so that often in regions of low temperature, such as the evaporator, two phases exist; while at high temperature regions, such as the outlet of the compressor, a single phase exists. It is necessary that in cases where phase separation occurs, the resulting liquid phases are capable of flowing readily at the existing temperatures.

The pour point of the lubricant must be low in order that the oil will flow at the lowest temperatures encountered. This is particularly true in the case of lubricants prepared from paraffinic waxy oils which must be dewaxed to a sufficiently low pour point.

The oil must have a low vapor pressure at 400° F.

Since the motor compressor system is normally sealed, the oil must cause very little wear of the moving parts as the life of the equipment is dependent on the wear rate.

The lubricant must be stable at the highest temperatures reached in the system and nonreactive with the refrigerant in the presence of metals it contacts which may act as catalysts. The lubricant-refrigerant mixture also must not corrode metals such as iron or copper which are normally present.

Generally, refrigeration oils are based upon hydrocarbon oils obtained from petroleum and highly refined. They may be derived from naphthenic or paraffinic crudes, and each type has advantages and disadvantages. The petroleum-derived oils must be dewaxed to yield a low pour point oil. They must be highly refined to eliminate components which can react with chlorine-containing refrigerants to liberate hydrogen chloride.

Alkylbenzenes have been suggested as lubricants for refrigeration equipment. U.S. Pat. 3,092,981 teaches the use of alkylbenzenes or blends of alkylbenzenes with conventional oil for the lubrication of refrigeration compressors. The alkylbenzenes are superior to conventional oils in compatibility with the refrigerant and in thermal stability. However, a practical disadvantage of alkylbenzenes is the low viscosity of those which are actually available; that is, the alkylbenzenes containing up to about 25 carbon atoms in the alkyl chain. Refrigeration oils are classified on the basis of the viscosity at 100° F., and grades having nominal viscosities of 80, 100, 150, 200, 300 and 500 SUS (Saybolt Universal seconds) are provided. Most refrigeration equipment requires the grades covering the range from 150 to 500 SUS. Alkylbenzenes with alkyl side chains containing from 18 to 25 carbon atoms generally have viscosities in the range of about 60 to 120

SUS and thus are of too low viscosity to be generally useful.

SUMMARY OF THE INVENTION

In accordance with the present invention there is provided a new class of refrigeration lubricating oil consisting essentially of alklylbenzene having one or more side chains of 1 to 25 carbon atoms and containing a total of from 10 to 25 carbon atoms in the alkyl groups and from about 2 to about 50% by weight of polyisobutylene having a viscosity in the range of from about 3,000 to about 1,000,000 SUS at 100° F.

The refrigerating lubricating oil compositions of this invention are readily obtainable and free of shortcomings associated with the lubricants of the prior art. These lubricants are readily prepared by blending relatively low molecular weight alkylbenzenes with highly viscous polymers of isobutylene. The alkylbenzenes, which are generally available, may contain from 1 to 25 carbon atoms in each of the alkyl groups and may contain more than one alkyl side chain with a total of from 10 to 25 carbon atoms in the alkyl groups. Usually, except for methyl radicals, there will not be more than two alkyl groups in the molecule.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The isobutylene polymer is added to the alkylbenzene to increase the viscosity in the range required for a refrigerator lubricant. It should have a viscosity at 100° F. of from 3,000 SUS to 1,000,000 SUS. The concentration required depends on the viscosities of the alkylbenzene and the isobutylene polymer and is generally in the range of 2% to 50% of the total.

The alkylbenzene used in preparing this refrigeration lubricant has alkyl groups containing a total of from 10 to 20 carbon atoms, and these may have either a branched chain or a straight chain configuration. Such compounds may be prepared by various well known methods, but it is preferred to alkylate benzene with an olefin or with an alkyl halide in the presence of an appropriate catalyst, such as hydrogen fluoride or aluminum chloride. The alkylbenzene should be esentially free of normal paraffins or other waxy-like materials which will raise the pour point. While alkylbenzenes prepared from straight chain olefins derived by cracking paraffin wax are not excluded, those having branched alkyl side chains are preferred. (Thus, the alkyl groups should be derived preferably from polypropylene or polybutylene.)

The polymerized isobutylene used in these refrigeration lubricants is prepared in the usual way by the catalytic polymerization of isobutene. A wide range of molecular weights is available, but only those polymers having a viscosity of 3,000 SUS to 1,000,000 SUS at 100° F. are useful in this formulation. Preferably, the polymerized isobutylene has a viscosity in the range of 40,000 SUS to 150,000 SUS at 100° F.

The refrigerator lubricant of the invention may contain additives of the types conventionally used. These include foam inhibitors, such as silicone polymers; metal deactivators, such as alizarine, quinizarine, Schiff bases, alkyl sulfides, zinc dithiocarbamates, and mercaptobenzothiazole; oxidation inhibitors, such as dibutyl-p-cresol; and scavengers for hydrogen chloride, such as epoxides.

The following examples illustrate the refrigeration lubricating oils according to the present invention. These examples are in no manner intended to limit the invention described. Unless otherwise indicated, percentages are on a weight basis.

A number of compositions were prepared and subjected to tests to determine their value as refrigerator lubricants. Three different alkylbenzenes were blended with an isobutylene polymer to prepare lubricants of the 300 viscosity grade (nominal 300 SUS at 100° F.). The isobutylene polymer had a molecular weight of 1,400 (number average) and a viscosity at 100° F. of 123,000 SUS. It is sold by Chevron Chemical Company as Chevron Polybutene 32. A description of the blends follows:

Oil A

The alkylbenzene used was prepared by alkylating benzene with a propylene polymer blend in which 80% of the material fell in the range of 15 to 19 carbon atoms. The resulting alkylbenzene had a molecular weight of 320. A blend was prepared consisting of 78.4% of this material and 21.6% of the polybutene.

Oil B

The alkylbenzene used was prepared by alkylating benzene with a propylene polymer blend having from 15 to 23 carbon atoms. The molecular weight of the product was 328. A blend of 85.5% of the alkylbenzene and 14.5% of the polybutene was prepared.

Oil C

The alkylbenzene was prepared by alkylating benzene with a propylene polymer of which 82% fell in the range of 12 to 15 carbon atoms. The resulting alkylbenzene had a molecular weight of 263. A blend of 69.4% of this material and 30.6% of the polybutene was prepared.

The above oil blends conforming to the invention were compared with the alkylbenzene used in Oil B but without the addition of any butylene polymer. This is referred to as Oil D. The blends were also compared with a commercial conventional refrigerator lubricant which was of the highly refined naphthenic type derived from petroleum. This is referred to as Oil E. The data on all five refrigerator lubricants are presented in Table I.

TABLE I

Tests	Method	Oil A	Oil B	Oil C	Oil D	Oil E
Color, Gardner	ASTM D 1540	<1	<1	<1	<1	5
Viscosity, SUS:						
100° F.	ASTM D 445	309.8	307.8	307.3	121.4	291.5
210° F.	ASTM D 2161	50.6	50.5	55.2	39.0	47.1
Viscosity index	ASTM D 2270	75	75	112	55	29
Pour point, °F.	ASTM D 97	−35	−35	−35	−40	−35
Pour point (10% oil plus 90% Freon 12), °F.		<−100	<−100	<−100	<−100	<−100
Freon floc, ° F [1]		−80	−100	<−100	−95	−80
High temperature stability:						
Appearance of liquid	Elsey: Refrigerating Engineering, July 1952, pp. 737–42	Essentially water white				Black
Copper plating on steel strip		Trace	(2)	(2)	(2)	(3)
Etching of copper wire	One week at 175° C.	(4)	Trace	Trace	Trace	(3)
Shell four-ball wear test, scar diameter, mm	1,800 r.p.m., 5 kg., 75° C., one hour.	0.232	0.284	0.353	0.377	0.417
Dielectric strength, 77° F., kv	ASTM D 877	35+	35+	35+	32	30

[1] A mixture of 9 ml. of Freon 12 (dichlorodifluoromethane) and 1 ml. of lubricating oil is cooled at a rate of about 1° F. per minute. The temperature at which a solid substance separates as a floc is determined.
[2] Some.
[3] Substantial.
[4] None.

The oils conforming to the invention have higher viscosity indexes than either Oils D or E, which represent prior art lubricants. The oils of the invention are also superior in high temperature stability, as measured by the Elsey test procedure, and are superior in wear characteristics, as demonstrated by the Shell Four-Ball Wear Test.

Refrigerator oils conforming to the invention and in the viscosity range of the nominal 150 and 500 grades were prepared. These oil blends were prepared from the same alkylbenzenes and polybutene used in Oils A, B and C. The compositions of these oils are as follows:

Oil F—89% alkylbenzene of Oil A and 11% polybutene.
Oil G—96% alkylbenzene of Oil B and 4% polybutene.
Oil H—80% alkylbenzene of Oil C and 20% polybutene.
Oil I—71% alkylbenzene of Oil A and 29% polybutene.
Oil J—78% alkylbenzene of Oil B and 22% polybutene.
Oil K—64% alkylbenzene of Oil C and 36% polybutene.

The test data obtained on these oils are listed in Table II.

TABLE II

Tests	Oil F	Oil G	Oil H	Oil I	Oil J	Oil K
Viscosity, SUS:						
100° F.	151	158	145	518	502	474
210° F.	42.1	----------	43.6	63.5	59.9	54.2
Viscosity index	65	----------	105	93	78	107
Pour point, ° F.	−40	−40	−45	−40	−40	−40
Freon floc, ° F.	−75	−90	<−90	−55	<−90	<−90
High temperature stability:						
Appearance of liquid	Essentially water white					
Copper plating on steel strip [1]	Better	Better	[2]	Better	Better	[3]
Etching of copper wire [1]	[3]	[3]	[3]	Better	[4]	[3]
Dielectric strength, 77° F., kv.	35+	26	35+	35+	35+	33

[1] Compared to a standard petroleum base oil (Oil E in Table I).
[2] Slightly poorer.
[3] Same.
[4] Poorer.

The effect of the molecular weight and viscosity of the polymerized isobutylene was investigated. The same alkylbenzenes were used as in the previous experiments. Chevron Polybutene 32 was replaced by a polyisobutylene of lower viscosity and by one of higher viscosity. These isobutylene polymers are marketed by Chevron Chemical Company under the names Polybutene 24 and Polybutene 128. Polybutene 24 has a molecular weight (number average) of 950 and a viscosity at 100° F. of 40,000 SUS. Polybutene 128 has a molecular weight (number average) of 2,700 and a viscosity at 100° F. of 890,000 SUS.

The following oils were prepared from the alkylbenzenes and Polybutene 24 and Polybutene 128:

Oil L—74% alkylbenzene of Oil A and 26% Polybutene 24.
Oil M—82.1% alkylbenzene of Oil A and 17.9% Polybutene 128.
Oil N—82.1% alkybenzene of Oil B and 17.9% Polybutene 24.
Oil O—89% alkylbenzene of Oil B and 11% Polybutene 128.
Oil P—63.6% alkylbenzene of Oil C and 36.4% Polybutene 24.
Oil Q—76.3% alkylbenzene of Oil C and 23.7% Polybutene 128.

The test data obtained on these oils are listed in Table III.

TABLE III

Tests	Oil L	Oil M	Oil N	Oil O	Oil P	Oil Q
Viscostity, SUS:						
100° F.	297	309	298	304	298	306
210° F.	50.6	54.3	48.9	51.0	52.5	57.9
Viscosity index	82	107	58	82	99	126
Pour point, ° F.	−35	−40	−35	−35	−40	−40
Freon floc, ° F.	−75	−70	<−85	<−85	<−85	−70
High temperature stability:						
Appearance of liquid	Essentially water white					
Copper plating on steel strip [1]	Better	Better	Better	Better	Better	[2]
Etching of copper wire [1]	Better	[3]	[3]	[3]	Better	[2]
Dielectric strength, 77° F., kv.	35+	35+	35+	34	35+	35+

[1] Compared to a standard petroleum base oil (Oil E in Table I).
[2] Slightly poorer.
[3] Same.

Oils of the invention were prepared from alkylbenzenes having linear alkyl groups derived from paraffin. These alkylbenzenes were blended with Polybutene 32 to yield the following oils:

Oil R

An alkylbenzene being essentially monoalkyl and containing from 11 to 14 carbon atoms with an average molecular weight of 255 was blended with polybutene so that the blend contained 58.5% alkylbenzene and 41.5% Polybutene 32.

Oil S

An alkylbenzene similar to that used in Oil R but containing from 10 to 13 carbon atoms and having an average molecular weight of 236 was blended so that the final oil contained 56.5% alkylbenzene and 43.5% Polybutene 32.

Oil T

An alkylbenzene similar to that used in Oil R but containing from 10 to 15 carbon atoms and having an average molecular weight of 259 was blended so that the final oil contained 59% alkylbenzene and 41% Polybutene 32.

The test data obtained on these oils are listed in Table IV.

TABLE IV

Tests	Oil R	Oil S	Oil T
Viscosity, SUS:			
100° F.	313	286	323
210° F.	59.6	56.5	61.1
Viscosity index	127	128	132
Pour point, ° F.	−55	−50	−45
Freon floc, ° F.	<−90	<−85	<−85
High temperature stability:			
Appearance of liquid	Water white		[1]
Copper plating on steel strip [2]	Better	Better	Better
Etching of copper wire [2]	Better	Better	[3]
Dielectric strength, 77° F., kv.	35	35	35

[1] Slightly yellow.
[2] Compared to a standard petroleum base oil (Oil E in Table I).
[3] Same.

A refrigeration lubricant according to the invention was tested for friction reducing properties in a tribometer. This is a device in which a cast iron pad slides over a cast iron

disk, and the apparatus was operated at a temperature of 250° F. and at sliding velocities similar to those encountered in refrigerant compressors. Static friction (zero velocity) is important in a compressor because of the reciprocating nature of piston travel.

The lubricant used was a blend of 74% of alkylbenzene similar to that used in Oil A and 26% Polybutene 24. It had a viscosity at 100° F. of 286 SUS and was designated RO 300. The friction characteristics of this lubricant as indicated by Coefficient of Friction (ratio of horizontal force to the vertical force) are compared in Table V with the petroleum-derived lubricant, Oil E.

TABLE V

	Friction	
Velocity (ft./min.)	RO 300	Oil E
0	0.17	0.27
0.03	0.18	0.29
0.06	0.18	0.26
0.10	0.17	0.24
0.3	0.17	0.19
0.5	0.16	0.18
1.0	0.16	0.17
10	0.14	0.15

The data show that the refrigerator lubricant of the invention has a decidedly lower coefficient of friction and is superior to conventional petroleum-based lubricants in friction-reducing properties in the critical region of low sliding velocities. This correlates with the low wear resultng in the Shell Four-Ball Wear Test illustrated in Table I. These desirable lubricity properties are surprising since synthetic oil refrigerator lubricants have previously been poor compared to conventional mineral oil compositions.

The oxidation stability of the refrigeration lubricant according to the invention was also tested using the method outlined in ASTM D 1934 both with and without copper catalyst. In this method the test material is contacted with oxygen for a period of 96 hours at 115° C. Changes in Gardner color, neutralization number (mg. KOH/g.) were observed.

TABLE VI

Tests	RO 300		Oil E	
Color, Gardner	<1		4-5	
Viscosity, SUS:				
100° F.	286		202	
210° F.	50.2		47.1	
Viscosity index	83		29	
Pour point, ° F.	−35		−35	
Neutralization number, mg. KOH/g	0.01		0.01	
Oxidation test, 96 hr. at 115° C.:	No Cu	Cu	No Cu	Cu
Color, Gardner	2	2	7	
Neutralization No., mg. KOH/g	0.06	0.06		13 0.04

In the above table, RO 300 is illustrative of the refrigeration lubricant compositions of the invention. Oil E, as previously mentioned, is a standard petroleum base oil used for comparison.

The above tests show that the refrigeration lubricant compositions of the invention have particularly desirable oxidation resisting properties. As indicated by the color test, very little change occurs with the alkylbenzene and polyisobutylene composition of RO 300 whereas the standard petroleum base Oil E gives a substantially increased darkening in color, even more so in the presence of copper. Also the above tests show that the neutralization number of both oils is practically nil.

The solubility of lubricant RO 300 was determined in both Freon 12 (dichlorodifluoromethane) and Freon 22 (monochlorodifluoromethane). At all temperatures up to 200° F., two phases existed; one essentially Freon and the other oil rich. The oil-rich phase was found to consist predominantly of polybutene with a low concentration of the alkylbenzene which remained dissolved in the Freon. Surprisingly, the presence of the separate phase of the viscous polybutene did not interfere with the operation of the refrigerating equipment.

While the character of this invention has been described in detail with numerous examples, this has been done by way of illustration only and without limitation of the invention. It will be apparent to those skilled in the art that modifications and variations of the illustrative examples may be made in the practice of the invention within the scope of the following claims.

What is claimed is:

1. A lubricating oil composition for refrigeration systems consisting essentially of alkylbenzene having one or more side chains of 1 to 25 carbon atoms and containing a total of from about 10 to about 25 carbon atoms in the alkyl groups and from about 2 to about 50% by weight of polyisobutylene having a viscosity in the range of from about 3,000 to about 1,000,000 SUS at 100° F.

2. The composition according to claim **1** in which the polyisobutylene has a viscosity in the range of from about 40,000 to about 150,000 SUS at 100° F.

3. The composition according to claim **2** in which the alkylbenzene has a total of from about 10 to about 20 carbon atoms in the alkyl groups.

4. The composition according to claim **3** in which the alkylbenzene has not more than 2 alkyl groups other than methyl radicals.

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