

June 11, 1963

C. R. BEGEMAN ETAL

3,092,981

REFRIGERATION APPARATUS

Original Filed Aug. 9, 1955

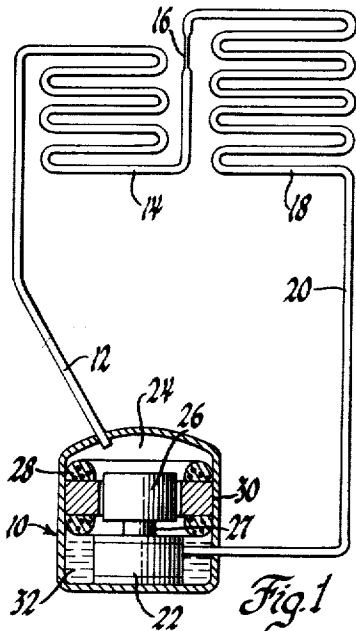


Fig. 1

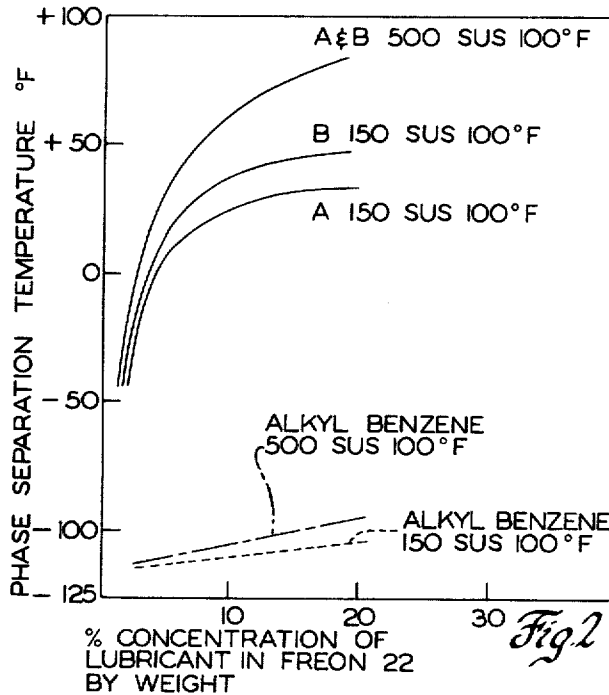


Fig. 2

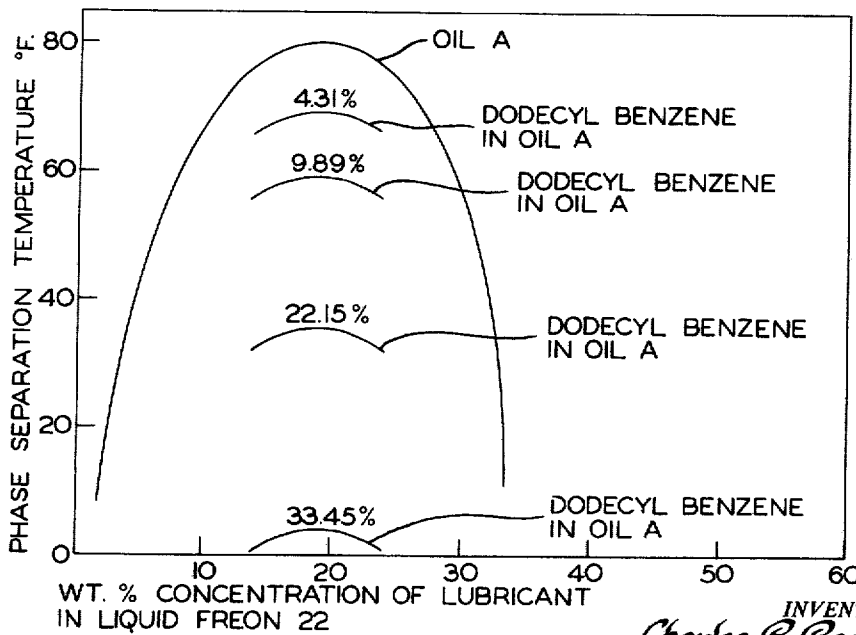


Fig. 3

INVENTORS
*Charles R. Begeman &
Victor A. Williams*
Peter P. Kozak
ATTORNEY

1

2

3,092,981

REFRIGERATION APPARATUS

Charles R. Begeman, Grosse Pointe Woods, Mich., and Victor A. Williamitis, Dayton, Ohio, assignors to General Motors Corporation, Detroit, Mich., a corporation of Delaware

Continuation of application Ser. No. 527,216, Aug. 9, 1955. This application July 15, 1960, Ser. No. 43,149 7 Claims. (Cl. 62-468)

This invention relates to refrigeration apparatus and particularly to refrigeration apparatus of the sealed compressor type wherein the lubricant which lubricates the moving parts of the refrigeration apparatus comes into direct contact with the refrigerant, and relatively small portions of which are carried with the refrigerant throughout the refrigeration cycle.

This is a continuation of the United States patent application Serial No. 527,216, filed August 9, 1955, now abandoned and assigned to the assignee of the present application.

It is an object of this invention to provide a working fluid for a refrigeration apparatus which includes a refrigerant capable of being in liquid and gaseous phases within the operating temperature range of the refrigeration apparatus and a wax-free lubricant which is completely soluble in the refrigerant and is highly thermally stable within the refrigeration apparatus in the range of the operating temperatures thereof.

It is another object of this invention to provide a working fluid for a refrigeration apparatus which includes a lubricant comprising an alkyl benzene and a refrigerant wherein the refrigerant is completely miscible with the alkyl benzene and is capable of existing in liquid and gaseous phases within the operating temperature range of the refrigeration apparatus.

It is a further object of this invention to provide a working fluid for a refrigeration apparatus which includes a refrigerant of a fluoro halo derivative of an aliphatic hydrocarbon capable of being in liquid and gaseous phases within the operating temperature range of the refrigeration apparatus and a lubricant comprising alkyl benzene.

It is yet another object of this invention to provide a refrigeration apparatus which includes a motor compressor, a condenser, an expansion device and evaporator in fluid flow relationship and a working fluid which includes a fluoro halo derivative of an aliphatic hydrocarbon and a lubricant comprising an alkyl benzene.

Further objects and advantages of the present invention will be apparent from the following description, reference being had to the accompanying drawings wherein preferred embodiments of the present invention are clearly shown.

In the drawings:

FIGURE 1 is a diagrammatic representation of one type of refrigeration apparatus embodying this invention.

FIGURE 2 is a graph comparing "Floc" points or phase separation temperatures of various refrigeration lubricants and alkyl benzenes at various concentrations in Freon 22.

FIGURE 3 is a graph comparing phase separation temperatures or "Floc" points of a refrigeration lubricant and the same lubricant containing various amounts of dodecyl benzene at various concentrations in Freon 22.

A refrigeration apparatus embodying this invention is diagrammatically indicated in FIGURE 1. A motor compressor unit 10 discharges compressed refrigerant, carrying some lubricant, through a pipe 12, to a condenser 14. The condensed refrigerant and lubricant then passes to an expansion device such as capillary tube 16 and then to an evaporator 18. The mixture of lubricant and vaporized

refrigerant flows through suction line 20 to the compressor 22 of the motor compressor unit 10 wherein the vapor is compressed and discharged into dome 24 of the motor compressor unit. The compressed vapor is then discharged through pipe 12 for recirculation through the refrigeration apparatus. The compressor 22 is driven by an electric motor comprising a rotor 26 operatively connected to the compressor 22 by shaft 27 and a stator 28 secured to the containing member 30 of the motor compressor unit. The compressor 22 is preferably partially submerged in a body of lubricant 32 held in containing member 30 for lubricating the moving parts of the compressor. As above indicated, circulating refrigerant comes in direct contact with the lubricant in the motor compressor unit and carries small amounts of lubricant therewith throughout the refrigeration cycle. In operation, the temperature in the refrigeration apparatus may vary from about -100° F. at the end of the capillary tube or expansion device to about 400° F. at the compressor outlet.

Although the refrigeration apparatus described is of the high side type, i.e., the refrigerant enters containing member 30 directly at the compressor so that the fluid in dome 24 is under considerable pressure, it will be obvious that the present invention is also applicable to low side or other types of refrigeration apparatus.

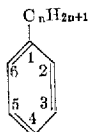
The refrigerant used in the present invention preferably comprises a fluoro halo derivative of an aliphatic hydrocarbon of the character disclosed in the patent to Midgeley et al., Re. 19,265, reissued August 7, 1934, as, for example, trichlorofluoromethane (Freon 11), dichlorodifluoromethane (Freon 12) and particularly difluoromonochloromethane (Freon 22).

The lubricant which is associated with the refrigerant throughout the refrigeration cycle has presented serious problems to satisfactory refrigeration operation in connection with certain otherwise useful refrigerants. One requirement of a satisfactory refrigeration lubricant which may be associated with a refrigerant to constitute a working fluid for a refrigeration apparatus of the type described, is that the lubricant be substantially free of wax so as to eliminate wax precipitation in and consequent blocking or restricting of the capillary tube and/or expansion valves at the low temperatures attained therein, a condition prevalent in conventional refrigeration lubricating oils such as mineral oils. Various attempts have been made to dewax or refine mineral oils which are effective in minimizing wax precipitation when used with certain refrigerants such as Freon 12. However, such oils are ineffective in various degrees when used at very low temperatures with F-12 or at any temperatures with a refrigerant such as Freon 22 in which such oils are not completely soluble. A further requirement of a suitable refrigeration lubrication is that it be completely soluble in the particular refrigerant used throughout the range of operating temperatures whereby oil "logging" of the evaporators be minimized so as to eliminate the need for trapping out or removing the lubricant circulating with the refrigerant. Another important requirement is that the lubricant have a high degree of chemical and thermal stability in the presence of the refrigerant, the metals, and motor insulation materials with which the lubricant comes in contact and is sealed for the life of the refrigeration apparatus.

It has been discovered that a combination of properties which substantially meet the above requirements exist in oils which may be described chemically as alkyl benzenes. The term "alkyl benzenes" as used herein includes hydrocarbon compounds having a single aromatic ring, one or more hydrogen atoms of which have been replaced by hydrocarbon group or groups consisting of a saturated aliphatic chain or chains, i.e., substituted benzenes where-

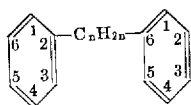
in the substituent groups are nonaromatic radicals derived from alkanes having the general formula C_nH_{2n+1} . The alkyl benzenes as used herein also include compounds having two or more benzene rings joined by an alkyl group.

The alkyl benzene lubricant referred to may consist of monosubstituted benzenes in which a single hydrogen atom on the benzene ring has been replaced by an alkyl group which may be described by the following generalized structural formula.



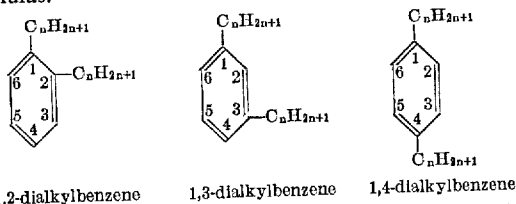
Specific compounds which may be named include, for example, dodecyl benzene, pentadecyl benzene, hexadecyl benzene and heptadecyl benzene.

Compounds having two benzene rings joined by an alkyl group may be described by the following generalized formula



Specific compounds which may be named include, for example, diphenyl decane, diphenyl dodecane and diphenyl pentadecane.

The alkyl benzene lubricant may also consist of a benzene ring having two or more hydrogen atoms substituted by alkyl groups wherein the orientation of the substituent groups may be in the ortho, meta or para positions of the benzene groups as shown by the following generalized formulas.

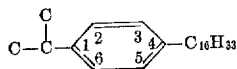


1,2-dialkylbenzene 1,3-dialkylbenzene 1,4-dialkylbenzene

Similarly, in the case of trialkylbenzenes the substituent alkyl groups may be orientated to constitute, for example, 1,3,5-trialkylbenzene, 1,2,3-trialkylbenzene or 1,2,4-trialkylbenzene and in the case of tetraalkylbenzenes, the substituent groups may be orientated to constitute, for example, 1,2,3,4-tetraalkylbenzene, 1,3,4-tetraalkylbenzene, and 1,2,4,5-tetraalkylbenzene.

For the purposes of the present invention, the alkyl groups on the benzene rings may include from 1 to about 50 carbon atoms per group. These alkyl groups may have either a normal, i.e., straight chain configuration or a branched chain configuration.

Although it may be convenient in many cases to prepare alkyl benzenes with identical substituent groups, it is not necessary that the alkyl groups be identical. For example, a suitable compound is 4-hexadecylcumene.



A suitable refrigeration lubricant may consist of a mixture of monoalkylbenzenes or a mixture of monoalkylbenzenes and polyalkylbenzenes or a mixture of polyalkylbenzenes with or without compounds having two or more benzene rings joined by alkyl groups. The compounds are selected preferably so as to have a viscosity range of from 50 to 2000 seconds Saybolt (SUS) measured at 100° F., the exact viscosity selected being dependent on the operating characteristics and the particular refrigerant of the refrigeration apparatus. Alkyl benzenes having viscosity properties within this range will contain from

16 to 42 carbon atoms per molecule and will have an average molecular weight of from 246 to 582.

The superiority of the alkyl benzenes of the present invention with respect to solubility thereof in refrigerants is illustrated by the graph shown in FIGURE 2. The solubility of refrigeration lubricants is generally measured by mixing various percentages of oil and refrigerant in a glass-pressure apparatus and externally cooling the same until phase separation is noted. This phase separation is sometimes termed the "Floc" point of the oil. The graph of FIGURE 2 shows the temperature of the phase separation plotted against concentration in Freon 22 and compares the phase separation or "Floc" points at various concentrations of two of the best and most soluble oils currently used by the refrigeration industry with typical "cuts" of alkyl benzenes. The refrigerant used in the comparison is Freon 22 (difluoromonochloromethane) since solution of oil in this refrigerant is more difficult than in other refrigerants.

The oil designated as "A" is a commercial refrigerant type naphthenic oil having the following specifications:

	525 vis.	150 vis.	ASTM method
Flash point, ° F., min.....	370	330	D-92-46.
Fire point, ° F., min.....	430	370	D-92-46.
Viscosity at 100° F. SUS.....	500-560	150-160	D-88-44.
Pour point, ° F., not above.....	-10	-35	D-97-39.
Color NPA, not darker than.....	2	1 1/2	D-155-45T.
Specific gravity at 60° F.....	.922-.934	.910-.922	D-287-39.
Floc test (90% F-12+10% oil by vol.), ° F.....	-30	-70	

The oil designated as "B" is a commercial refrigerant type naphthenic oil having the following specifications:

	500 vis.	150 vis.	ASTM method
Flash point, ° F., min.....	370	330	D-92-52.
Fire point, ° F., min.....	430	370	D-92-52.
Viscosity at 100° F.....	500-560	150-160	D-88-44.
Viscosity at 210° F., min.....	-20	-40	D-97-47.
Pour Point, ° F., not above.....	-20	-40	
Color NPA, not darker than.....	2	1 1/2	
Specific gravity at 60° F.....	.912-.919	.892-.910	D-287-52.
Floc test (haze) (90% F-12+10% oil by vol.) not above ° F.....	-35	-60	

The "Floc" points are compared for concentration of oil of from 1% to 20% in Freon 22. The "Floc" points of A and B oils of viscosity 500 SUS at 100° F. vary from -30° F. to 84° F. The "Floc" point for "A" oil of viscosity 150 SUS at 100° F. varies from -30° F. to 34° F. and for the "B" oil of the same viscosity from -45° F. to 46° F. In contrast for alkyl benzenes having a viscosity of 500 SUS at 100° F., the "Floc" point varies from below -100° F. to -90° F. and for alkyl benzenes of viscosity 150 SUS at 100° F. the "Floc" point is below -100° F. for the same concentration range. The "Floc" points for alkyl benzenes related to concentration is shown in FIGURE 2 in broken lines since exact values were not determined below -100° F.

The "Floc" tests above described have been generally accepted as indicating low temperature performance of lubricants. However, these tests have been found to give only a partial indication of performance. To determine actual performance of the working fluid, particularly under conditions where very small amounts of wax in the lubricant are detrimental to refrigeration apparatus performance, actual tests set up with a specially modified test apparatus consisting of a 1/2 H.P. compressor and a 0.026" capillary restriction tube operating with Freon 22 indicated that after two hours operation lubricants under identical conditions of concentration and viscosity tested as follows: oil "A" would block or restrict the capillary at 0° F., oil "B" at -40° F., and alkyl benzenes at -80° F. Thus, the use of alkyl benzenes as a lubricant in

5

refrigeration apparatus of the type described represents a substantial improvement in the operation thereof as the apparatus may be operated at lower temperatures with improved results. As above indicated, solubility and wax-freedom of an oil for refrigeration purposes are highly important, particularly for the prevention of blocking or restricting of capillary tube and/or expansion valves. Oil "logging" of evaporators is also minimized by the use of highly soluble lubricants in the refrigerants. The properties of solubility and wax-freedom are evidenced to a high degree by the alkyl benzenes.

As indicated above, another important requirement of a good refrigeration oil is a high degree of chemical and thermal stability. The above "A" and "B" oils and alkyl benzenes of comparable viscosity were compared by sealing the lubricant, refrigerant and metal catalysts in pressurized glass tubes and exposing the combination to high temperatures. A comparison of alkyl benzenes to the best accepted refrigeration oils is as follows:

Oil	Thermal exposure	Color after thermal exposure	Refrigerant decomposed in milligrams of released chlorine
A.....	2 weeks at 400° F..	Black tar.....	Various tests 100 to 385.
B.....do.....	Deep brown.....	35.
Alkyl benzenes.....do.....	Clear amber.....	12.

In general, refrigeration compressors operated with alkyl benzenes operate smoothly and display the same superiorities indicated by the above measurements. The alkyl benzenes used in the above measurements are distillation cuts from a mixture of monoalkyl benzenes and dialkyl and trialkyl benzenes. The alkyl groups in these compounds may vary in size from C_4H_9 to $C_{15}H_{31}$ and have branched configurations.

It has also been found that the alkyl benzenes may be added to conveniently used oils to improve their properties for use as a refrigeration lubricant. FIGURE 3 shows the effect on the phase separation or the "Floc" point at various concentrations of adding dodecyl benzene to oil "A" and is illustrative of the effect of adding alkyl benzenes to conventionally used lubricants. Thus, for a concentration of 22.5% of oil "A" in Freon 22, the 22.5% solubility point is 84° F. whereas when the lubricant in the same concentration includes 4.31%, 9.89%, 22.15% and 33.45% by weight of dodecyl benzene, this point is depressed to 73° F., 58° F., 34° F., and 4° F., respectively. Thus, the alkyl benzenes of the present invention may be added to conventional refrigeration lubricants in various proportions to improve their properties as refrigeration lubricants.

While the embodiments of the present invention as herein disclosed constitute preferred forms, it is to be understood that other forms might be adopted.

We claim:

1. A refrigerating apparatus of the sealed compressor type comprising a compressor, condenser and evaporator in refrigerant flow relationship, and a working fluid within said apparatus in contact with moving parts of said compressor which require lubrication, said working fluid consisting essentially of a refrigerant and a chemically inert, wax-free lubricant soluble in said refrigerant, said refrigerant being a fluoro halo substituted hydrocarbon selected from the class consisting of methane and ethane and being in the liquid and gaseous phases within the operating temperatures of said refrigerating apparatus, said lubricant being present in an amount sufficient to lubricate the moving parts of said compressor and comprising an alkyl benzene in which the alkyl groups contain 1 to about 50 carbon atoms and having a viscosity of about 50 to 2,000 seconds Saybolt measured at 100° F.

2. A refrigerating apparatus of the sealed compressor type comprising a compressor, condenser and evaporator

6

in refrigerant flow relationship, and a working fluid within said apparatus in contact with moving parts of said compressor which require lubrication, said working fluid consisting essentially of a refrigerant and a chemically inert, wax-free lubricant soluble in said refrigerant, said refrigerant being a fluoro halo substituted hydrocarbon selected from the class consisting of methane and ethane and being in the liquid and gaseous phases within the operating temperatures of said refrigerating apparatus, said lubricant being present in an amount sufficient to lubricate the moving parts of said compressor and comprising a mixture of monoalkyl, dialkyl and trialkyl benzenes in which the alkyl groups contain 1 to about 50 carbon atoms and having a viscosity of about 50 to 2,000 seconds Saybolt measured at 100° F.

3. A refrigerating apparatus of the sealed compressor type comprising a compressor, condenser and evaporator in refrigerant flow relationship, and a working fluid within said apparatus in contact with moving parts of said compressor which require lubrication, said working fluid consisting essentially of a refrigerant and a chemically inert, wax-free lubricant soluble in said refrigerant, said refrigerant being difluorodichloromethane and being in the liquid and gaseous phases within the operating temperatures of said refrigerating apparatus, said lubricant being present in an amount sufficient to lubricate the moving parts of said compressor and comprising an alkyl benzene in which the alkyl groups contain 1 to about 50 carbon atoms and having a viscosity of about 50 to 2,000 seconds Saybolt measured at 100° F.

4. A refrigerating apparatus of the sealed compressor type comprising a compressor, condenser and evaporator in refrigerant flow relationship, and a working fluid within said apparatus in contact with moving parts of said compressor which require lubrication, said working fluid consisting essentially of a refrigerant and a chemically inert, wax-free lubricant soluble in said refrigerant, said refrigerant being difluorodichloromethane and being in the liquid and gaseous phases within the operating temperatures of said refrigerating apparatus, said lubricant being present in an amount sufficient to lubricate the moving parts of said compressor and comprising a mixture of monoalkyl, dialkyl and trialkyl benzenes in which the alkyl groups contain 1 to about 50 carbon atoms and having a viscosity of about 50 to 2,000 seconds Saybolt measured at 100° F.

5. A refrigerating apparatus of the sealed compressor type comprising a compressor, condenser and evaporator in refrigerant flow relationship, and a working fluid within said apparatus in contact with moving parts of said compressor which require lubrication, said working fluid consisting essentially of a refrigerant and a chemically inert, wax-free lubricant soluble in said refrigerant, said refrigerant being a fluoro halo substituted hydrocarbon selected from the class consisting of methane and ethane and being in the liquid and gaseous phases within the operating temperatures of said refrigerating apparatus, said lubricant being present in an amount sufficient to lubricate the moving parts of said compressor and comprising an alkyl benzene containing about 16 to 24 carbon atoms per molecule having a viscosity of about 50 to 2,000 seconds Saybolt measured at 100° F.

6. A refrigerating apparatus of the sealed compressor type comprising a compressor, condenser and evaporator in refrigerant flow relationship, and a working fluid within said apparatus in contact with moving parts of said compressor which require lubrication, said working fluid consisting essentially of a refrigerant and a chemically inert, wax-free lubricant soluble in said refrigerant, said refrigerant being a fluoro halo substituted hydrocarbon selected from the class consisting of methane and ethane and being in the liquid and gaseous phases within the operating temperatures of said refrigerating apparatus, said lubricant being present in an amount sufficient to lubricate the moving parts of said compressor and com-

7

prising alkyl benzenes having an average molecular weight of from about 246 to 582 having a viscosity of about 50 to 2,000 seconds Saybolt measured at 100° F.

7. A refrigerating apparatus of the sealed compressor type comprising a compressor, condenser and evaporator in refrigerant flow relationship, and a working fluid within said apparatus in contact with moving parts of said compressor which require lubrication, said working fluid consisting essentially of a refrigerant and a chemically inert, wax-free lubricant soluble in said refrigerant, said refrigerant being a fluoro halo substituted hydrocarbon selected from the class consisting of methane and ethane and being in the liquid and gaseous phases within the operating temperatures of said refrigerating apparatus, said lubricant being capable of remaining in a liquid phase at about -80° F. and being present in an amount sufficient to lubricate the moving parts of said compressor, said lubricant comprising alkyl benzenes in which the alkyl groups contain 1 to about 50 carbon atoms and

8

having a viscosity of about 50 to 2,000 seconds Saybolt measured at 100° F. and an average molecular weight of about 246 to 582.

References Cited in the file of this patent

UNITED STATES PATENTS

167,181	Mallory	Aug. 31, 1875
1,735,170	Kucher	Nov. 12, 1929
2,008,680	Carlisle et al.	July 23, 1935
2,138,775	Towne	Nov. 29, 1938
2,187,388	Williams	Jan. 16, 1940
2,523,863	Cook et al.	Sept. 26, 1950
2,550,113	Flowers	Apr. 24, 1951
2,666,744	Dixon	Jan. 19, 1954
2,824,061	Davidson et al.	Feb. 18, 1958
2,912,383	Huth	Nov. 10, 1959

FOREIGN PATENTS

467,874	Great Britain	June 24, 1937
---------	---------------	---------------