

REFRIGERATING APPARATUS AND REFRIGERANT COMPRESSOR

1 BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a refrigeration cycle and refrigerant compressor, and it relates to, in particular, a refrigeration-cycle-constituting material system comprising a refrigerating machine oil composition suitable for a flon type refrigerant containing no chlorine and having a critical temperature of 40°C or higher, for example, flon 134a, and electrical insulating materials and a drying agent which are hardly deteriorated by the refrigerating machine oil composition.

Prior Art

In recent years, chlorine-containing flons (chlorofluorocarbons, abbreviated as CFC) have been included in the list of compounds under regulation in use, all over the world because of the problems of environmental pollution, in particular, the ozone depletion and the global warming.

20 All of flons included in the list of compounds under regulation in use are chlorine-containing flons such as flon 11, flon 12, flon 113, flon 114, flon 115, etc. Flon 12 which has been exclusively used as a refrigerant in refrigerating apparatus such as



1 refrigerators, dehumidifiers, etc., has also been  
included in the list.

Therefore, a refrigerant usable in place of  
flon 12 is required. Hydrofluorocarbon (HFC) having a  
5 low reactivity with ozone and a short decomposition  
period in the air has recently been noted as a  
substitute refrigerant. Flon 134a (1,1,1-tetrafluoro-  
ethane,  $\text{CH}_2\text{FCF}_3$ ) is a typical example of such a  
refrigerant. In detail, when the ozone depletion  
10 potential (ODP) of flon 12 (dichlorodifluoromethane  
 $\text{CCl}_2\text{F}_2$ ) is taken as 1, that of flon 134a is zero. When  
the global warming potential (GWP) of flon 12 is taken  
as 1, that of flon 134a is 0.3 or less. Flon 134a is  
noncombustible and similar to flon 12 in thermal  
15 properties such as temperature-pressure characteristics.  
Therefore, flon 134a has been said to be advantageous in  
that it can be put into practical use without greatly  
changing the structures of refrigerating apparatus such  
as refrigerators and dehumidifiers and refrigerant  
20 compressors in which flon 12 has heretofore been used.

Flon 134a, however, has a unique chemical  
structure and hence very characteristic properties.  
Therefore, it has a very poor compatibility with  
refrigerating machine oils such as mineral oils and  
25 alkylbenzene oils which have been used in conventional  
refrigeration system using flon 12, and hence it cannot  
be put into practical use at all. In addition, the  
suitability including the improving effect on the



1 lubrication and the resistance to frictional wear of the  
sliding portions of compression mechanical parts, the  
influence on electrical insulating materials, the  
influence on drying agents, etc. is a problem, and there  
5 has been an eager desire for the development of a novel  
material system constituting a compressor and a  
refrigerating apparatus.

Therefore, before referring to the problem of  
the miscibility of a refrigerant with a refrigerating  
10 machine oil, conventional refrigerant compressor and  
refrigeration apparatus which use a flon type  
refrigerant are first explained with reference to Fig. 7  
to Fig. 9.

Fig. 7 is a vertical cross-sectional view of  
15 the principal part of a conventional closed rotary  
compressor. Fig. 8 is a cross-sectional view for  
explaining the displacement volume of the compressor  
section of the compressor. Fig. 9 is a diagram showing  
the structure of an ordinary refrigeration cycle.

20 In Fig. 7, numeral 1 shows a case used both as  
a closed container and as a oil pan. In the case 1, an  
electric motor section 22 and a compressor section 23  
are accommodated.

The electric motor 22 is composed of a stator  
25 19 and a rotor 20, and a rotating shaft 4A made of cast  
iron is fitted in the rotor 20. The rotating shaft 4A  
has an eccentric portion 3 and an shaft hole 17 is



1 formed in hollow form on the one side of the eccentric  
portion 3.

The core wire of the winding wire portion 19a  
of the stator 19 is coated with an ester imide film, and  
5 an electrical insulating film of a polyethylene  
terephthalate is inserted between the core portion and  
the winding wire portion of the stator. The rotor 4A  
has a surface finished by grinding.

The compressor 23 has as its chief mechanism  
10 components a cylinder 2 made of an iron-based sintered  
product; a roller 7 made of cast iron which is fitted in  
the eccentric portion 3 of the rotating shaft 4A and  
eccentrically rotated along the inside of the cylinder  
2; a high-speed steel vane which is reciprocated in the  
15 groove 8 of the cylinder 2 while one side of the vane is  
in contact with the roller 7 and the other side is  
pushed by a spring 9; and a main bearing 5 and a sub-  
bearing 6 which are made of cast iron or an iron-based  
sintered product, are provided on both ends of the  
20 cylinder, and serve both as bearings for the rotary  
shaft 4A and as the side wall of the cylinder 2.

The sub-bearing 6 has a discharge valve 27,  
and a discharge cover 25 is attached thereto so as to  
form a silencer 28. The main bearing 5, the cylinder 2  
25 and the sub-bearing 6 are fastened with a bolt 21.

A pump chamber 12 is composed of a space and  
parts surrounding the space, i.e., the back of the vane



1 10, the groove 8 of the cylinder 2, the main bearing 5  
and the sub-bearing 6.

The main bearing 5 has a suction piece 14  
which can suck a naphthene type or alkylbenzene type  
5 refrigerating machine oil 13A in which a refrigerant  
flon gas stored in the bottom of the case 1 has been  
dissolved, into the pump chamber 12. The sub-bearing 6  
has a discharge port 16 which can discharge the  
refrigerating machine oil 13A to an oil tube 15 from the  
10 pump chamber 12. The oil tube 15 is designed to be able  
to supply the refrigerating machine oil 13A to the shaft  
hole 17 of the rotating shaft 4A and then to predeter-  
mined sliding portions from the shaft hole 17 through a  
branch opening 18.

15 The action of the rotary compressor thus  
composed is explained below with reference to Figs. 7  
and 8. When the compressor is operated to rotate the  
rotating shaft 4A made of cast iron, a roller 7 made of  
tempered cast iron is rotated with the rotation of  
20 rotating shaft 4A, and the high-speed steel vane 10 is  
reciprocated in the groove 8 of the cylinder 2 made of  
cast iron or a iron-based sintered product while the  
vane 10 is pushed by the spring 9 and its end is in  
contact with the roller 7. Thus, the vane 10 compresses  
25 a refrigerant (flon 12) which has flown in through a  
refrigerant suction opening (not shown), and the  
refrigerant is discharged outside the compressor from a  
discharge pipe 29 through a refrigerant discharge



1 opening 24. The winding wire portion 19a and the  
electrical insulating film (not shown) of the stator 9  
are immersed in the refrigerating machine oil containing  
flon dissolved therein, or they are exposed to circum-  
5 stances of spraying with mist of the refrigerant oil.

In the case of a combination of a conventional  
refrigerating machine oil consisting of a mineral oil or  
an alkylbenzene and flon 12, flon 12 is completely  
miscible with the refrigerating machine oil in all use  
10 ranges, so that it has been not necessary at all to care  
about the various problems concerning the miscibility of  
flon 134a with a refrigerating machine oil which are  
hereinafter described in detail, namely, the separation  
into two layers between the refrigerating machine oil  
15 and the refrigerant in a compressor, and the residence  
of the refrigerating machine oil in a heat exchanger.  
However, in the case of fluorohydrocarbon type  
refrigerants containing no chlorine which have unique  
characteristics, for example, flon 134a, the miscibility  
20 of the refrigerant with a refrigerating machine oil is  
the most serious problem in practice because there is no  
practical refrigerating machine oil which can easily  
dissolve the refrigerant.

In general, for improving the performance  
25 characteristics of a compressor, namely, the coefficient  
of performance (COP) which indicates the energy  
efficiency, it has been necessary to minimize the



1 mechanical loss of the compressor and maximize its  
volumetric efficiency.

The mechanical loss of a refrigerant  
compressor mainly includes the friction loss at the  
5 journal bearing and thrust bearing in the mechanical  
part and the power for agitating oil. In general, it  
has been said that the best means is to minimize the  
value of the coefficient of friction ( $\mu$ ) defined by the  
following equation on the basis of the hydrodynamic  
10 lubrication theory of a journal bearing:

$$\mu = 2\pi^2(D/C)\eta N/P \quad (9)$$

wherein      N : revolution rate,  
              P : pressure on surface,  
               $\eta$  : viscosity,  
              D : diameter of shaft,  
15            C : diametral clearance.

This fact indicates that in a refrigerant  
compressor operated under hydrodynamic lubrication  
conditions, not only the structural factors regarding  
dimensions and shapes but also the actual viscosity of a  
20 refrigerating machine oil containing flon dissolved  
therein which is a factor influenced by operation  
circumstances, have a close relationship to the  
mechanical loss of the compressure.

On the other hand, for keeping the volumetric  
25 efficiency highest, it is necessary that in a mechanical



1 chamber for compressing a refrigerant gas, the leakage  
of the refrigerant gas from the high pressure side to  
the low pressure side should be prevented by carrying  
out sealing between parts which works to compress the  
5 refrigerant gas. It should be noted that also in this  
case, the actual viscosity of a refrigerating machine  
oil containing the refrigerant dissolved therein has an  
important function.

As described above, in a refrigerant  
10 compressor heretofore used by the use of flon 12 and a  
refrigerating apparatus using the refrigerant  
compressor, it is important for the improvement of  
performance characteristics of the compressor to  
optimize the actual viscosity of a refrigerating machine  
15 oil containing the refrigerant dissolved therein, at a  
rated operation point under usual operation conditions.

A refrigerating apparatus such as a  
refrigerator or a dehumidifier is operated, though in  
rare cases, in a high-temperature circumstance much more  
20 severe than usual operation conditions. In this case,  
the lubrication in the apparatus gets into a so-called  
boundary lubrication region in which a lubricating oil  
layer is thined, so that the metal surfaces of sliding  
portions of a bearing are brought into contact with each  
25 other. Consequently, the coefficient of friction is  
increased at once, resulting in heat generation.  
Therefore, scoring or seizing-and-adhesion phenomenon  
occurs between the bearing and a rotating shaft and



1 deteriorates the reliability of a refrigerant  
compressor. Therefore, some consideration is needed for  
preventing a fatal problem from occurring even under  
boundary lubrication conditions. In a conventional  
5 refrigerant compressor using flon 12, chlorine in flon  
12 acts effectively as an extreme pressure agent. In  
detail, when scoring or seizing-and-adhesion phenomenon  
takes place between a bearing and a rotating shaft, the  
refrigerant flon 12 dissolved in a refrigerating machine  
10 oil as bearing-lubricating oil is decomposed by  
frictional heat generated by the scoring or the  
phenomenon, and chlorine, i.e., the decomposition  
product, reacts with iron on the surface of the bearing  
to form iron chloride which acts as a lubricant.

15 As described above, in the case of a  
refrigerating apparatus using a high-pressure vessel  
type rotary compressor, for example, a refrigerator, a  
refrigerant compressor and a refrigerating apparatus  
which satisfy the operation conditions at an ambient  
20 temperature of 30°C described below are satisfactory in  
the coefficient of performance indicating energy  
efficiency and the reliability of a product, and most  
products have been used in such ranges. The discharge  
pressure of the compressor: about 10 kg/cm<sup>2</sup>abs, oil  
25 temperature: about 100°C, refrigerating machine oil: an  
alkylbenzene oil or a mineral oil having a viscosity at  
40°C of 56 cSt and a viscosity at 100°C of 6 cSt, the  
actual viscosity of which becomes 1 to 4 cSt.



1           On the other hand, in the case of a refriger-  
 ating apparatus using a low-pressure vessel type  
 reciprocating compressor (the explanation of the  
 structure and operation is omitted), for example, a  
 5   refrigerator, there have been used a refrigerant  
 compressor and a refrigerating apparatus which satisfy  
 the following operation conditions at an ambient  
 temperature of 30°C; the suction pressure of the  
 compressor: about 1.6 kg/cm<sup>2</sup> abs, oil temperature: 85°C,  
 10   refrigerating machine oil: a mineral oil having a  
 viscosity at 40°C of 8 to 15 cSt and a viscosity at  
 100°C of 1.8 to 4.2 cSt, the actual viscosity of which  
 becomes 2 to 6 cSt.

Next, a fundamental refrigeration cycle  
 15   provided with a refrigerant compressor which thus sucks,  
 compresses and then discharge a flon type refrigerant,  
 is explained below with reference to Fig. 9.

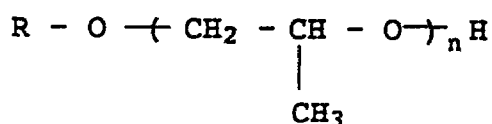
As shown in Fig. 9, a compressor 40 compresses  
 a low-temperature, low-pressure refrigerant gas,  
 20   discharges the resulting high-temperature, high-pressure  
 refrigerant gas and send the same to a condenser 41.  
 The refrigerant gas sent to the condenser 41 becomes a  
 high-temperature, high-pressure refrigerant fluid while  
 releasing its heat to the air, and then it is sent to an  
 25   expansion mechanism (e.g. an expansion valve or a  
 capillary tube) 42 while being freed from water by a  
 dryer 45. The high-temperature, high-pressure  
 refrigerant fluid which passes the expansion mechanism



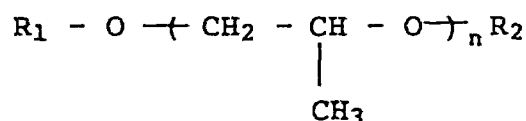
1 becomes low-temperature, low-pressure wet vapor owing to  
squeezing effect and is sent to an evaporator 43. The  
refrigerant introduced into the evaporator 43 is  
evaporated while absorbing heat from the surroundings,  
5 and the low-temperature, low-pressure gas which has come  
out of the evaporator 43 is sucked into the condenser  
40. Thereafter, the above cycle is repeated.

As there frigerant, flon 12 has heretofore  
been used. However, the employment of flon 12 is under  
10 regulations, as described above. The employment of flon  
134a in place of flon 12 involves many problems because  
conventional mineral oil type or alkylbenzene type  
refrigerating machine oils for flon 12 are very poor in  
miscibility with flon 134a. Therefore, refrigerating  
15 machine oils having a good miscibility with flon 134a  
have been vigorously developed and various refrigerating  
machine oils have been proposed. As typical examples of  
such refrigerating machine oils, there are known the  
compounds having ether linkages exemplified below.

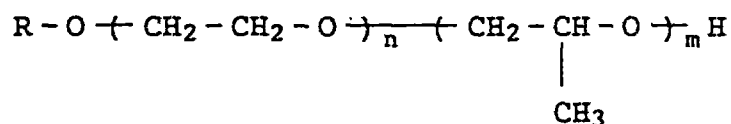
20 For example, Japanese Patent Application Kokai  
No. 1-259093 discloses "a refrigerating machine oil for  
a flon compressor" which comprises as base oil a  
propylene glycol monoether represented by the general  
formula:



- 1 wherein R is an alkyl group having 1 to 8 carbon atoms,  
and n is an integer of 4 to 19; Japanese Patent  
Application Kokai No. 1-259094 discloses a diether type  
compound obtained by etherifying one end of propylene  
5 glycol which is represented by the general formula:



- wherein each of R<sub>1</sub> and R<sub>2</sub> is an alkyl group having 1 to 8  
carbon atoms, and n is an integer (average molecular  
weight: 300 to 600); and Japanese Patent Application  
Kokai No. 1-259095 discloses a monoether type compound  
10 which is a copolymer of propylene glycol and ethylene  
glycol and is represented by the general formula:



- wherein R is an alkyl group having 1 to 14 carbon atoms,  
and m and n are integers, the ratio m: n being 6: 4 to  
1 : 9 (average molecular weight: 300 to 2,000).  
15 The difference of these polyalkylene glycols  
from conventional mineral oils and alkylbenzene oils  
have been reported as follows. By the introduction of  
ether linkages into the molecule, the affinity for flon  
134a is enhanced to improve the miscibility with flon  
20 134a greatly, refrigerant lubrication due to the  
phenomenon of separation into two layers (a phenomenon



1 that the refrigerant and the refrigerating machine oil  
are insoluble in each other and separate; hereinafter  
referred to merely as "two-layer separation") in the  
sliding portions of a compressor can be prevented, the  
5 return of the oil to the compressor which is induced by  
residence phenomenon due to the adhesion of the oil to  
the inner wall of a heat exchanger can be suppressed,  
and there can be solved the problems concerning the  
reliability of the compressor and a refrigerating  
10 apparatus, for example, seizing and scoring in the  
sliding portions of the compressor.

Such compounds thus containing a large number  
of ether linkages (C-O-C), however, are disadvantageous  
in that,

15 (1) they have a saturation water absorption  
rate is high (they tend to absorb water).

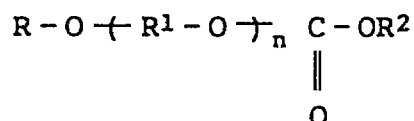
(2) they have a low volume resistivity.

(3) they have a low oxidation stability, so  
that the total acid value is apt to be increased.

20 Therefore, the compounds have been not suitable for  
refrigerant compressors and refrigerating apparatus in  
which a hermetic motor is used as an electric motor.  
That is, although the compounds have an improved  
miscibility with the refrigerant, they are dis-  
25 advantageous in that they attack the insulating  
materials of the motor to deteriorate the electrical  
insulating characteristics. In all of the above  
compounds, the end group having an ether linkage is



1 capped with hydrogen, and the hydrogen further increases  
the hygroscopicity. Therefore, it has been proposed to  
replace the hydrogen by an ester group to obtain a  
refrigerating machine oil represented by the following  
5 formula (see Japanese Patent Application Kokai No.  
2-132178):



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wherein R is a hydrocarbon group, R<sup>1</sup> is an alkylene R<sup>2</sup>  
is an alkyl group, and n is an integer which is such  
that the viscosity of this compound becomes 10 to 300  
10 (at 40°C).

However, the improved miscibility with the  
refrigerant of this compound is also brought about by a  
large number of ether linkages in the molecule, like  
that of the above compounds, and hence this compound  
15 involves the same problems as in the case of the above  
compounds.

Thus, the compounds having ether linkages tend  
to absorb water because of the above problem (1), and  
the compounds themselves are hydrolyzed by the water to  
20 become unstable. Furthermore, the water freezes, chokes  
the capillary of a refrigeration cycle, and disturbs the  
pressure balance. The volume resistivity of the  
compounds is low as described as the problem (2), so  
that the electrical insulating properties are  
25 deteriorated. When the total acid value is increased as

1 described as the problem (3), the compounds are  
hydrolyzed to become unstable.

As described above, flon 134a which is used as  
a substitute refrigerant for conventional refrigerant  
5 flon 12 involves the following fatal problem. Because  
of its unique molecular structure, flon 134a has a low  
affinity for mineral oil type and alkylbenzene oil type  
refrigerating machine oils which have heretofore been  
used, and hence it lacks miscibility with the  
10 refrigerating machine oils which is essential in a  
refrigerant compressor and a refrigerating apparatus.

Attempts have been made to improve the  
miscibility, but have been accompanied with, for  
example, the deterioration of the electrical insulating  
15 properties, the water problem, and the instability  
problems, such as the hydrolysis and the decomposition  
of the compound by an acid. Each problem is described  
below in more detail.

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#### SUMMARY OF THE INVENTION

20 (1) A refrigerating machine oil having a bad  
miscibility cannot be put into practical use in a  
refrigerant compressor and a refrigerating apparatus  
from the viewpoint of performance characteristics and  
reliability, as described below.

25 In general, when the solubility of a  
refrigerating machine oil in a refrigerant is low, oil  
discharged from a compressor is separated in a heat

1 exchanger and the oil component adheres to the wall  
surface to remain, so that the amount of oil which  
returns to the compressor is decreased. Consequently,  
the oil surface in the compressor is lowered and a so-  
5 called oil drying-up phenomenon takes place, so that the  
oiling level is lowered.

When a compressor is exposed to a low-  
temperature circumstance in a refrigerating apparatus  
enclosing a large amount of a refrigerant, the following  
10 trouble is caused. In a so-called lying-idle state in  
which liquid refrigerant is present preferentially in  
the bottom of the compressor, low-viscosity liquid  
refrigerant which is present in the bottom as a result  
of two-layer separation is supplied to the sliding  
15 surface of a rotating shaft, so that the assurance of a  
lubricating oil film becomes difficult, resulting in  
damage to the compressor.

On the other hand, as to the refrigerating  
apparatus, a refrigerating machine oil which has  
20 separated adheres to the inner wall of an evaporator  
having a low temperature, to form a heat-insulating  
layer, and therefore it inhibits the heat-transferring  
capability seriously. Moreover, when this refrigerating  
machine oil of wax form chokes an expansion mechanism (a  
25 capillary tube) or a piping, the amount of the  
refrigerant circulated is greatly decreased, resulting  
in a lowered cooling power. As to the compressor, the  
pressure of sucked gas is lowered and the pressure of



1 discharged gas is increased. Therefore, the heat  
deterioration of the refrigerating machine oil and  
damage to bearings are caused, so that the long-term  
reliability of the refrigerant compressor and the  
5 refrigerating apparatus is greatly deteriorated.

Accordingly, a first object of the present  
invention is to solve such conventional problems and  
provide a refrigerating apparatus and a refrigerant  
compressor which are provided with a refrigerating  
10 machine oil which is highly miscible with and hence  
suitable for flon type refrigerants containing no  
chlorine a typical example of which is flon 134a. More  
specifically, the present invention is fundamentally  
intended to make improvements with respect to, for  
15 example, (1) water absorption properties, (2) volume  
resistivity, and (3) oxidative deterioration, and seek  
for a novel refrigerating machine oil composition which  
is miscible with flon 134a under all operation condi-  
tions of a refrigerant compressor and a refrigerating  
20 apparatus. It is also intended to provide a refrige-  
ration system having excellent performance character-  
istics, efficiency and reliability in refrigerating  
apparatus and refrigerant compressors which are  
different in purposes, by developing at least the  
25 following two refrigeration oils: a refrigeration oil  
for moderate-temperature refrigerating apparatus such as  
dehumidifiers which achieves a first aim, i.e.,  
attainment of a critical solution temperature of 0°C or



1 lower; and a refrigeration oil for low-temperature  
refrigerating apparatus such as refrigerators which  
achieves a second aim, i.e., attainment of a critical  
temperature of  $-30^{\circ}\text{C}$  or lower.

5 (2) In the long run, it is beneficial to the  
prevention of global warming (GWP) to enhance the  
coefficient of performance (COP) (which indicates the  
energy efficiency, i.e., the ratio of the cooling power  
of a refrigerant compressor to an input) under usual use  
10 conditions under which refrigerant compressors and  
refrigerating apparatus are usually operated.

For reducing the input to a compressor in  
order to improve the performance characteristics of the  
compressor, it is necessary to reduce the coefficient  
15 of friction on the basis of the hydrodynamic lubrication  
theory of coaxial bearing. For the reduction, it is  
necessary to measure the solubility of flon 134a in the  
refrigerating machine oil used in the present invention  
and thereby determine the optimum value of the actual  
20 viscosity of the oil used in the compressor. When the  
actual viscosity is thus optimized, the coefficient of  
friction of a bearing becomes minimum and the  
coefficient of performance of the compressor and a  
refrigerating apparatus using the compressor becomes  
25 maximum.

Therefore, a second object of the present  
invention is to attain high performance characteristics  
and a high reliability by specifying a viscosity range

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1 of the refrigerating machine oil which is most suitable  
for a refrigerating apparatus using a high-pressure  
vessel type rotary compressor or a low-pressure vessel  
type reciprocating compressor, on the basis of the above  
5 bearing theory.

(3) However, although very rarely in practice,  
there is carried out an extremely severe operation such  
as operation in a high-temperature circumstance or  
overload operation which are more severe than expected  
10 by a designer. Also in this case, a sufficient  
reliability should be assured.

In a compressor using flon 134a, scoring or  
seizing of the sliding portion of a bearing of the  
compressor tends to take place more often than in a  
15 compressor using a conventional refrigerant flon 12, in  
a so-called boundary lubrication region (in which  
contact between metal surfaces occurs) beyond the  
hydrodynamic lubrication region of a coaxial bearing.

When contact between metal surfaces takes  
20 place in the sliding portion of a bearing, flon 12  
dissolved in an oil is decomposed to form a conversion  
coating of iron chloride on an iron-based sliding  
frictional surface. This iron chloride acts as an  
extreme pressure agent to suppress the adhesion and  
25 seizing.

On the other hand, since flon 134a is a  
refrigerant containing no chlorine, chlorine cannot  
possibly be supplied to a compressor using flon 134a.



1 Therefore, unlike flon 12, flon 134a is hardly expected  
to have the above action as extreme pressure agent.

Accordingly, a third object of the present  
invention is to provide a refrigerating apparatus and a  
5 refrigerant compressor in which by using a flon type  
refrigerant containing no chlorine represented by flon  
134a and a refrigerating machine oil containing an  
extreme pressure agent, the prevention of scoring and  
seizing of the sliding portions and the assurance of  
10 sufficient reliability can be achieved even when the oil  
runs out in the sliding bearing of the compressor and  
extremely severe operation is carried out.

(4) A fourth object of the present invention is to  
provide a refrigerant compressor and a refrigerating  
15 apparatus which use a composition comprising a flon type  
refrigerant containing no chlorine represented by flon  
134a and a refrigerating machine oil, and have an  
electrical insulating system wherein electrical insulat-  
ing materials such as an electrical insulating film and  
20 an insulation-coated winding wire which constitute an  
electric motor section have a sufficient long-term  
reliability.

(5) Flon 134a has a high water absorption rate and  
refrigerating machine oils miscible with flon 134a are  
25 relatively hydrophilic though fairly improved. There-  
fore, both of them tend to carry water into a refrigera-  
tion cycle. Water in a refrigerating apparatus is  
frozen in an evaporator on the low-temperature side and



1 chokes a pipe having a small diameter, such as a  
capillary tube to lower the refrigerating capability.  
Furthermore, in the long run, the refrigerating machine  
oil, the refrigerant, electribcal insulating materials,  
5 etc. undergo hydrolysis reaction, so that minus charact-  
eristics are brought about, for example, the production  
of an acidic substance and a lowering of the mechanical  
strength are induced.

Accordingly, a fifth object of the present  
10 invention is to provide a refrigerating apparatus in  
which a flon type refrigerant containing no chlorine  
represented by flon 134a and a refrigerating machine oil  
coexists, and which has a dryer packed with a drying  
agent effective in improving the reliability of the  
15 refrigerating apparatus by separating and adsorbing only  
water without absorbing the refrigerant.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a graph showing a two-layer  
separation temperature which illustrates the miscibility  
20 of flon 134a with each refrigerating machine oil.

Fig. 2 is a graph showing a relationship  
between the amount of water dissolved in each of various  
refrigerating machine oils and its volume resistivity.

Fig. 3 is a graph showing a relationship  
25 between the atual viscosity of each refrigerating  
machine oil and the coefficient of performance during

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1 rated operation of a high-pressure vessel type rotary  
compressor.

Fig. 4 is a graph showing a relationship  
between the actual viscosity and the coefficient of  
5 performance during rated operation of a low-pressure  
vessel type reciprocating compressor.

Fig. 5 is a graph showing a relationship  
between FALEX test using an iron-based frictional  
sliding surface and a high-pressure atmosphere friction  
10 test using an oil containing flon 134a dissolved  
therein.

Fig. 6 is a graph showing the abrasion loss  
caused by a FALEX test.

Fig. 7 is a vertical cross-sectional view of  
15 the principal part of a closed rotary compressor.

Fig. 8 is a vertical cross-sectional view of  
the principal part of the compression mechanical part of  
a rotary compressor.

Fig. 9 is a diagram showing the structure of  
20 the refrigeration cycle of a refrigerating apparatus.

#### PREFERRED EMBODIMENT OF THE INVENTION

1. The above first object of the present  
invention can be achieved by a refrigerating apparatus  
comprising a refrigeration cycle comprising at least a  
25 compressor, condensor, dryer, expansion mechanism and  
evaporator, a refrigerant compomsed mainly of a  
fluorocarbon type refrigerant containing no chlorine and



1 having a critical temperature of 40°C or higher, and a  
 refrigerating machine oil comprising as base oil an  
 ester oil of one or more fatty acids which contains at  
 least two ether linkages ( $\text{-O-C-}$ ) in the molecule and  

$$\begin{array}{c} \parallel \\ \text{O} \end{array}$$

5 has a viscosity at 40°C of 2 to 70 cSt and a viscosity  
 at 100°C of 1 to 9 cSt.

As described above, it is absolutely necessary  
 for the ester oil to be an ester of one or more fatty  
 acids which contains at least two ester linkages in the  
 10 molecule. Ester oils of one or more fatty acids which  
 have one ester linkage have a bad miscibility with the  
 refrigerant and hence cannot be used. The usable ester  
 oil of one or more fatty acids can be obtained by the  
 esterification reaction of an alcohol with one or more  
 15 fatty acids. As the alcohol, a polyhydric alcohol is  
 preferable. As the fatty acids, those having 1 to 6  
 carbon atoms are preferable. The fatty acids may be  
 either monobasic or polybasic. The ester oils include  
 hindered ester oils and complex ester oils. From the  
 20 viewpoint of the miscibility with the refrigerant, ester  
 oils having a branched-chain structure tend to be  
 preferable to ester oils having a straight-chain  
 structure. Examples of practical ester oils of one or  
 more fatty acids are given below by the general formulas  
 25 (1) to (5).

The ester oils represented by the formulas (1)  
 to (4) are hindered ester oils, and the ester oils



- 1 represented by the formula (5) are complex ester oils.

These ester oils may be used singly or in combination of two or more thereof. The refrigerating machine oil comprise at least 50 wt% of these ester oils as base oil, and the balance may be made up by other well-known refrigerating machine oils.



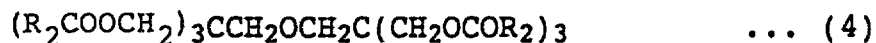
(examples of esters of neopentyl glycol (abbreviated as NPG) type alcohols which contain two ester linkages in the molecule).



- 10 (examples of esters of trimethylolalkylpropanes (abbreviated as TMP) which contain three ester linkages in the molecule).

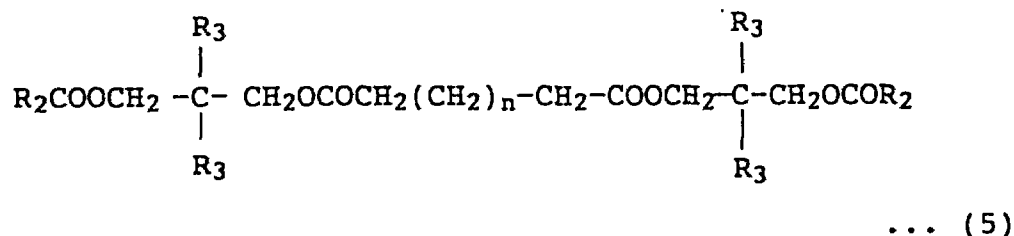


(examples of esters of pentaerythritol (abbreviated as PET) which contain 4 ester linkages in the molecule).



- 15 (examples of esters of dipentaerythritol (abbreviated as DPET) which contain 6 ester linkages in the molecule).





1 (examples of complex esters containing 4 or more ester linkages in the molecule).

In the above general formulas,  $\text{R}_1$  is H or an alkyl group having 1 to 3 carbon atoms,  $\text{R}_2$  is a straight  
 5 or branched-chain alkyl group having 5 to 12 carbon atoms,  $\text{R}_3$  is an alkyl group having 1 to 3 carbon atoms,  $\text{R}_3$  is an alkyl group having 1 to 3 carbon atoms, and  $n$  is an integer of 0 to 5.

The esters represented by the above general  
 10 formulas (1) to (4) are esters of polyhydric alcohols and monocarboxylic acids. As such esters, esters having a desired viscosity grade can be obtained by optionally choosing a combination of the alcohol and one or a plurality of the monocarboxylic acids and proportions of  
 15 these components.

As the complex esters represented by the general formula (5), esters having a high viscosity and a wide critical solution temperature range can be obtained by selecting the chemical structure of the  
 20 central dibasic acid (dicarboxylic acid) component from various chemical structures derived from succinic acid ( $n = 2$ ), glutaric acid (abbreviated as Glut), adipic acid (abbreviated as AZP), pimelic acid, suberic acid,



1 azelaic acid, and sebacic acid ( $n = 8$ ), selecting the  
polyhydric alcohol component and the terminal  
monocarboxylic acid component from various compounds,  
and varying the blending proportions (molar fraction).

5           The monocarboxylic acids represented by the  
formula  $R_2COOH$  may be straight- or branched-chain ones.  
The latter includes 2-ethylhexanoic acid (2EH), 2-  
methylhexanoic acid (i-C<sub>7</sub>), 3,5,5-trimethylhexanoic  
acid, 3,5-dimethylhexanoic acid (i-C<sub>8</sub>), 2-methyl-  
10 heptanoic acid. The monocarboxylic acids may be used  
singly or in combination of two or more thereof.

          The base oil of the refrigerating machine oil  
is prepared by adjusting the viscosity by using such  
hindered ester oils and complex ester is singly or in  
15 combination of two or more thereof.

          The refrigerant composed mainly of a fluoro-  
carbon type refrigerant containing no chlorine and  
having a critical temperature of 40°C or higher which is  
used in the present invention includes hydrofluoro-  
20 carbons and fluorocarbons. Specific examples of the  
hydrofluorocarbons are difluoromethane (R32), penta-  
fluoroethane (R125), 1,1,2,2-tetrafluoroethane (R134),  
1,1,1,2-tetrafluoroethane (R134a), 1,1,2-trifluoroethane  
(R143), 1,1,1-trifluoroethane (R143a), 1,1-difluoro-  
25 ethane (R152a) and monofluoroethane (R161). Specific  
examples of the fluorocarbons are hexafluoropropane  
(C216) and octafluorocyclobutane (C318). Of these,  
1,1,2,2-tetrafluoroethane (R134), 1,1,1,2-



44 15 11 51

1 tetrafluoroethane (R134a), 1,1,2-trifluoroethane (R143),  
 1,1,1-trifluoroethane (R143a) and hexafluoropropane  
 (C216) have a boiling point close to that of a  
 conventional refrigerant, dichlorodifluoromethane (R12),  
 5 and are preferable as substitute refrigerants. The  
 above-exemplified hydrofluorocarbon or fluorocarbon type  
 refrigerants can be used singly or as a mixture thereof.

The reason for the adjustment of critical  
 temperature of the refrigerant to 40°C or higher is that  
 10 there was required a refrigerating apparatus in which  
 the condensation temperature in a condenser was 40°C.

1) The above second object of the present  
 invention is, for one thing, achieved by a high-pressure  
 vessel type refrigerant compressor used in a  
 15 refrigeration cycle that comprises a closed vessel  
 stored with a refrigerating machine oil which  
 accommodates a motor composed of a rotor and a stator, a  
 rotating shaft fitted in the rotor, and a compressor  
 section connected to the motor through the rotating  
 20 shaft, and in which a high-pressure refrigerant gas  
 discharged from the compressor section resides, said  
 refrigerant being composed mainly of a fluorocarbon type  
 refrigerant containing no chlorine and having a critical  
 temperature of 40°C or higher, and said refrigerating  
 25 machine oil comprising as base oil an ester oil of one  
 or more fatty acids which contains at least two ester  
 linkages ( -O-C- ) in the molecule and has a viscosity



This Sheet Has Been Replaced



1 at 40°C of 2 to 70 cSt and a viscosity at 100°C of 1 to  
9 cSt.

The constitution of the ester oil of one or  
more fatty acids which contains at least two ester  
5 linkages in the molecule is as described above in  
detail.

In a high-pressure vessel type rotary  
compressor, for example, is previously enclosed the  
aforesaid refrigerating machine oil having a viscosity  
10 at 40°C of 2 to 70 cSt, preferably 5.0 to 32 cSt, so  
that the actual viscosity (at a gas pressure of 9 to 11  
kg/cm<sup>2</sup> abs and an oil temperature of about 100°C) of the  
oil which contains flon 134a dissolved therein may be  
1.0 to 4.0 cSt.

15 2) In addition, the above second object of the  
present invention is achieved by a low-pressure vessel  
type refrigerant compressor that comprises a closed  
vessel stored with a refrigerating machine oil which  
accommodates a motor composed of a rotor and a stator, a  
20 rotating shaft fitted in the rotor, and a compressor  
section connected to the motor through the rotating  
shaft, and from which a high-pressure refrigerant gas  
discharged from the compressor section is directly  
exhausted, said refrigerant being composed mainly of a  
25 fluorocarbon type refrigerant containing no chlorine and  
having a critical temperature of 40°C or higher, and  
said refrigerating machine oil comprising as base oil an  
ester of one or more fatty acids which contains at least



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1 two ester linkages  $\left( \begin{array}{c} -O-C- \\ || \\ O \end{array} \right)$  in the molecule and has

a viscosity at 40°C of 2 to 70 cSt and a viscosity at 100°C of 1 to 9 cSt.

5 The constitution of the ester oils of one or more fatty acids which contains at least two ester linkages in the molecule is as described above.

In a low-pressure vessel type reciprocating compressor, for example, is previously enclosed the aforesaid refrigerating machine oil having a viscosity  
10 at 40°C of 5.0 to 15 cSt and a viscosity at 100°C of 2.0 to 4.0 cSt, so that the actual viscosity (at a sucked gas pressure of 1.0 to 2.0 kg/cm abs and an oil temperature of 85°C) of the oil which contains flon 134a dissolved therein may be 2.0 to 4.5 cSt.

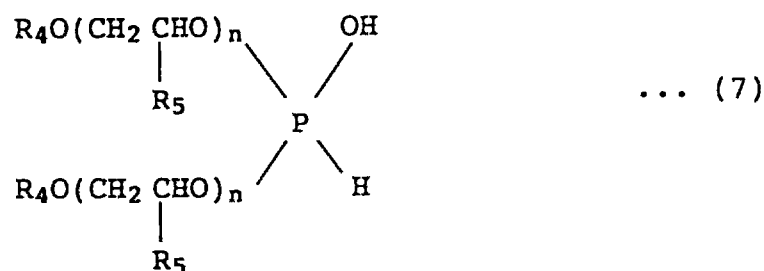
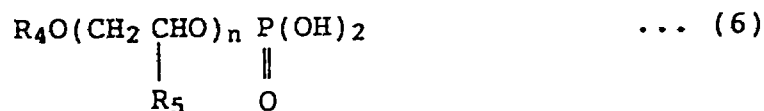
15 3) The above third object can be achieved by adding an extreme pressure agent to the aforesaid refrigerating machine oil.

The extreme pressure agent serves as an abrasion-preventing agent in sliding portions and  
20 includes, for example, alkylpolyoxyalkylene phosphate esters represented by the general formulas (6) and (7) and dialkyl phosphate esters represented by the general formula (8):

This Sheet Has Been Replaced



44-1191



- 1 wherein  $\text{R}_4$  is an alkyl group having 1 to 8 carbon atoms,  
and  $\text{R}_5$  is H or an alkyl group having 1 to 3 carbon  
(molecular weight: 400 to 700).



- wherein  $\text{R}_6$  is an alkyl group having 8 to 16 carbon  
5 atoms.

These phosphoric esters may be added singly or  
in combination of two or more thereof. The practical  
amount of the phosphoric esters added to the refrigerat-  
ing machine oil is 0.05 to 10 wt%.

- 10 It is also effective to add an acid-capturing  
agent, antioxidant, defoaming agent, etc. together with  
the extreme pressure agent (the abrasion-preventing  
agent).

- When an acid component is present in the  
15 refrigerating machine oil, the ester oil is decomposed

This Sheet Has Been Replaced



1 by the acid component to become unstable. Therefore,  
the acid-capturing agent is added for removing the acid  
component. For example, compounds such as epoxy  
compounds reactive with acids are preferable as the  
5 acids-capturing agent. Particularly preferable examples  
of the acid-capturing agent are compounds having an  
epoxy group and an ether linkage, for example,  
diglycidyl ether compounds such as polyalkylene glycol  
diglycidyl ethers; monoglycidyl ether compounds such as  
10 phenyl glycidyl ether; and aliphatic cyclic epoxy  
compounds. The reason is that the epoxy group of such a  
compound captures an acid and that the ether linkage  
contributes to the improvement of the miscibility of the  
refrigerating machine oil with the refrigerant to a  
15 certain extent.

The other additives described above are, for  
example, chlorine-capturing agents for preventing the  
influence of residues of, for instance, a chlorine-  
containing detergent used for producing the compressor  
20 or the refrigerating apparatus, additives for preventing  
oxidative deterioration during the circulation and  
storage of the oil, and additives for preventing  
foaming. These additives may be selected from those  
used in the conventional general techniques and are not  
25 critical in the present invention.

4) For achieving the fourth object, the  
insulating film constituting an electric motor section  
and the insulation-coated winding wire which are



described below are used in a refrigerating apparatus and a refrigerant compressor which simultaneously use a flon type refrigerant containing no chlorine represented by flon 134a and a refrigerating machine oil comprising as base oil the above-exemplified ester oil of one or more fatty acids. As the insulating film, there is used a crystalline plastics film having a glass transition temperature of 50°C or higher, or a composite film obtained by coating a film having a low glass transition temperature with a resin layer having a high glass transition temperature. As the insulation-coated winding wire, there is used an enameled wire having the enamel coating of a glass transition temperature of 120°C or higher, or an enameled wire having a composite coating consisting of a lower layer having a low glass transition temperature and an upper layer having a high glass transition temperature.

As the insulating film, for practical purposes, it is preferable to use at least one kind of insulating film selected from the group consisting of films of polyethylene terephthalates, polybutylene terephthalates, polypenylene sulfides, polyether ether ketones, polyethylene naphthalates, polyamide-imides and polyimides. As an enamel coating, it is preferable to use at least one kind of insulating layer selected from the group consisting of insulating layers of polyester imides, polyamides and polyamide-imides.

This Sheet Has Been Replaced



1        5)        For achieving the fifth object, a synthetic  
zeolite composed of a composite salt consisting of  
alkali metal silicates and alkali metal aluminates which  
has a pore diameter of 3.3 angstrom or less and a carbon  
5 dioxide gas absorption capacity (at 25°C and at a  
partial pressure of carbon dioxide gas of 250 mmHg) of  
1.0% or less, is used as a drying agent to be packed  
into the dryer, in the aforesaid refrigerating apparatus  
which simultaneously uses a flon type refrigerant  
10 containing no chlorine represented by flon 134a and a  
refrigerating machine oil comprising as base oil the  
above-exemplified ester oil of one or more fatty acids.

In a refrigerating apparatus comprising at  
least a compressor, condenser, expansion mechanism and  
15 evaporator, and using a flon type refrigerant containing  
no chlorine represented by flon 134a, the refrigerating  
machine oil according to the present invention which  
comprises at least one ester selected from the group  
consisting of hindered or complex esters containing two  
20 or more ester linkages in the molecule, and has a  
viscosity at 40°C of 2 to 70 cSt, preferably 5 to 32  
cSt, and a viscosity at 100°C of 1 to 9 cSt, preferably  
2 to 6 cSt, has a good miscibility with the refrigerant  
in the whole temperature ranges of the parts used in the  
25 refrigerating apparatus. Therefore, there is no two-  
layer separation between the refrigerant and the  
refrigerating machine oil. Accordingly, no two-layer  
separation is present in the oil-storing space in the



1 compressor, so that the supply of the oil to the sliding  
portions of hearings is assured, and flon gas discharged  
from the compressor is in a liquefied state by the  
condenser, namely, in a state in which the oil is always  
5 dissolved in flon 134a with a low viscosity in a low-  
temperature circumstance of  $-30^{\circ}\text{C}$  or lower in the  
evaporator. Thus, on the whole, the flon gas is in a  
low-viscosity state, so that the return of the oil to  
the compressor is improved.

10 Therefore, the lowering of oil surface in the  
compressor is prevented and hence the supply of the oil  
to the sliding portions of hearings can be assured.  
Thus, the problems causing scoring and seizing can be  
solved.

15 Furthermore, unlike conventional  
polyoxyalkylene glycol oils, the aforesaid refrigerating  
machine oil has a low saturated water-content of one-  
tenth or less as large as that of the conventional oils,  
a large improving effect on the stability to oxidative  
20 deterioration, and a volume resistivity of  $10^{13} \Omega\text{cm}$   
which is as high as that of an electrical insulating  
oil. Therefore, in a refrigerant compressor comprising  
a pressure vessel accommodating a motor section and a  
refrigerating apparatus using the refrigerant compres-  
25 sor, the refrigerating machine oil according to the  
present invention do not separate from flon 134a and has  
excellent characteristics with respect to both the  
performance characteristics and reliability of the



1 compressor. Since the refrigerating machine oil has an  
excellent miscibility also with conventional chlorine-  
containing flon refrigerants such as flon 12 and flon  
22, such conventional chlorine-containing refrigerants  
5 can, if necessary, be used in place of a portion of flon  
134a in admixture with flon 134a.

When the refrigerating machine oil according  
to the present invention which had an oil viscosity at  
40°C of 5 to 32 cSt was enclosed in a high-pressure  
10 vessel type rotary compressor and the coefficient of  
performance of the compressor was measured, the co-  
efficient of performance reached a peak in the case of  
using the oil which had a viscosity of 15 cSt. When the  
oil which had a viscosity of 5 to 32 cSt was used, the  
15 coefficient of performance was about 1.4 or more which  
corresponds to a value of 0.95 to 0.93 when the co-  
efficient of performance in the case of using a  
conventional combination of a flon 12 and an alkyl-  
benzene oil is taken as 1. Such a value indicates that  
20 the oil involves no practical problem. The refrigerat-  
ing machine oil according to the present invention which  
had a viscosity at 40°C of 56 cSt was found to be  
superior in the coefficient of performance of the  
compressor to polyoxypropylene glycol oils. The reason  
25 for this superiority is as follows. The ester linkages  
contained in the oil itself undergoes molecular orienta-  
tion mainly on the surfaces of iron-based sliding  
portions of the shaft and bearings of the compressor to



1 improve the lubrication. Moreover, the oil is decreased  
in actual viscosity owing to its high solubility in flon  
134a, to reduce the mechanical loss. These effects are  
synergistically brought about to improve the coefficient  
5 of performance of the compressor.

On the other hand, in the case of a low-  
pressure vessel type reciprocating compressor, the  
amount of flon 134a dissolved and the actual viscosity  
vary only in narrow ranges because the compressor is  
10 operated at a low pressure in the vessel of 1 to 2  
kg/cm<sup>2</sup> abs. Therefore, characteristics of a refrigerant  
and a refrigerating machine oil are hardly dependent on  
their kinds, and it was found that the oil which had a  
viscosity at 40°C of 5 to 15 cSt and a viscosity of  
15 100°C of 2 to 4 cSt was good in reliability and  
performance characteristics.

When the refrigerating machine oil according  
to the present invention is blended with an adequate  
amount (0.05 to 10 wt%) of an extreme pressure agent  
20 such as a strong primary or secondary phosphoric ester  
retaining OH groups in the molecule, for example, an  
alkylpolyoxyalkylene phosphate ester or a dialkyl  
phosphate ester, the resulting blend can push away a  
lubricating oil film having ester linkages undergoing  
25 molecular orientation on the surfaces of iron-based  
sliding portions constituting the shaft and bearings of  
the compressor, and form a stronger chemical adsorption  
film of the phosphoric ester. Therefore, the blend can



1 further improve the lubrication of the sliding portions  
to prevent scoring and seizing.

When the lubricating properties of the  
refrigerating machine oil according to the present  
5 invention containing the extreme pressure agent were  
examined, the critical seizing pressure on surface was  
greatly increased in a FALEX test (a seizing test on the  
oil) carried out without the dissolution of flon 134a in  
the oil. In addition, when there was measured the  
10 abrasion loss of an iron-based sliding member in the  
case of employment of the refrigerating machine oil  
containing the extreme pressure agent which further  
contained 50% of flon 134a dissolved therein, as simula-  
tion of the dissolution of a high concentration of flon  
15 134a, the abrasion loss could be reduced to one-fifth or  
less as large as that caused in the case of the oil  
which did not contain the extreme pressure agent. The  
suitable range of the amount of the extreme pressure  
agent added is 0.05 to 10 wt% as described above. The  
20 results of the abrasion loss test are as shown in Fig. 6  
though specifically described in the examples herein-  
after given. As shown in Fig. 6, the reducing effect of  
the addition of the extreme pressure agent on the  
abrasion loss is remarkable.

25 Conventional additives such as an acid-  
capturing agent, antioxidant, defoaming agent, etc. can  
be blended together with the extreme pressure agent.



1           Next, there are explained below electrical  
insulating materials for the refrigerant compressor  
using flon 134a together with the refrigerating machine  
oil according to the present invention. As an insulat-  
5 ing film used as electrical insulating material for the  
motor section, a crystalline plastics film having a  
glass transition temperature of 50°C or higher is used.  
The insulating film includes films of polyethylene  
terephthalates, polybutylene terephthalates, poly-  
10 phenylene sulfides, polyether ether ketones, poly-  
ethylene naphthalates, polyamide-imides and olyimides;  
and composite films obtained by coating a film having a  
low glass transition temperature with a resin layer  
having a high glass transition temperature. These films  
15 are hardly deteriorated in tensile strength character-  
istics and electrical insulating characteristics and  
involve no practical problem. This is because the films  
carry in a much smaller amount of water and produce a  
much smaller amount of an acid than do conventional  
20 polyoxyalkylene glycol oils, and hence are hardly  
deteriorated by hydrolysis of the films themselves.

          An enamel coating having a glass transition  
temperature of 120°C or higher is used on a magnet wire  
used in the motor section. The enamel coating includes,  
25 for example, monolayers of polyester imides, polyamides,  
polyamide-imides and the like, and composite enamel  
coating films obtained by forming an upper layer having



1 a high glass transition temperature on a lower layer  
having a low glass transition temperature. Like the  
above-mentioned films, these enamel coatings hardly show  
deterioration by hydrolysis, cracking, softening,  
5 swelling, a lowering of breakdown voltage, etc. and  
hence are useful for improving the reliability in  
practical. In some cases, a self-lubricating agent or  
an external lubricating agent is included in the enamel  
coating on the magnet wire, for imparting self-  
10 lubricating properties to improve the electrical  
workability. Fundamentally, the above characteristics  
of the enamel coating itself before the inclusion are  
retained.

Lastly, a drying agent packed into the dryer  
15 of the refrigerating apparatus in which flon 134a and  
the aforesaid refrigerating machine oil according to the  
present invention coexist is explained below. In this  
invention, it is preferable to use a synthetic zeolite  
composed of a composite salt consisting of alkali metal  
20 silicates and alkali metal aluminates which has a pore  
diameter of 3.3 angstrom or less, a carbon dioxide  
absorption capacity at 25°C and at a carbon dioxide  
partial pressure of 250 mmHg of 1.0% or less. As such a  
synthetic zeolite, XH-9 and XH-600 (trade names, mfd. by  
25 UNION SHOWA K.K.) can be exemplified. Both of them have  
a small fluorine ion adsorption. The same synthetic  
zeolite as above except for having a carbon dioxide gas  
adsorption capacity of 1.5% or more has a fluorine



1 adsorption of as large of 0.24% or more and hence  
possesses deteriorated adsorption characteristics and  
breaking strength as molecular sieves. Moreover,  
corroded crystal disintegration product of such a  
5 synthetic zeolite chokes the piping of the refrigeration  
cycle or injures the sliding portions of bearings of the  
compressor. When the pore diameter in the present  
invention is specified in relation to the above carbon  
dioxide adsorption capacity in consideration of such  
10 conditions, the troubles described above are not caused  
and it becomes possible to compose a highly reliable  
refrigerating apparatus.

Examples of the present invention are  
explained below with reference to Figs. 1 to 6 and  
15 Tables 1 to 4.

#### Examples 1 to 17

These examples show embodiments for achieving  
the above first object of the present invention. In a  
closed rotary compressor concerned with a refrigeration  
20 cycle and a refrigerant compressor, flon 134a was used  
as a refrigerant, and as a refrigerating machine oil,  
there was used each ester oil listed in Table 1 which  
contained two or more ester groups in the molecule and  
had a viscosity at 40°C of 2 to 70 cSt and a viscosity  
25 at 100°C of 1 to 9 cSt. For comparison, data on  
conventional refrigerating machine oils are also shown  
in Table 1.

This Sheet Has Been Replaced



1            Fig. 1 is a graph showing two-layer separation  
temperature which illustrates the miscibility of flon  
134a with each refrigerating machine oil. The graph was  
obtained by enclosing flon 134a and the refrigerating  
5 machine oil in a high-pressure glass vessel, observing  
visually the two-layer separation state at each tempera-  
ture and at each concentration of the refrigerating  
machine oil, and summarizing the observation results.  
The axis of abscissa refers to the concentration of the  
10 oil in flon 134a, and the axis of ordinate to tempera-  
ture. The first target value shown in Fig. 1 is a lower  
critical solution temperature necessary for a refrige-  
rating apparatus such as a dehumidifier, which has a  
moderate evaporator temperature ( $0^{\circ}\text{C}$  or lower). The  
15 second target value is a lower critical solution tem-  
perature necessary for a refrigerating apparatus such as  
a refrigerator, which has a low evaporator temperature  
( $-30^{\circ}\text{C}$  or lower). Both of the evaporator temperatures  
are specified values.

20            From Table 1, it can be seen that SUNISO 4GSD  
(a trade name, naphthene type) and Z300A (a trade name,  
alkylbenzene type) both manufactured by JAPAN SUN OIL  
Co., Ltd. were not dissolved. A polyalkylene glycol,  
PAG56 (a trade name, mfd. by JAPAN SUN OIL Co., Ltd.)  
25 had a lower critical solution temperature (shown by L1)  
of  $-60^{\circ}\text{C}$  and an upper critical solution temperature  
(shown by U1) of  $35^{\circ}\text{C}$ . The ester oils containing two or  
more ester groups in the molecule according to the



1 present invention are so excellent in critical solution  
temperatures that their lower critical solution tempera-  
ture (shown by L2) is  $-70^{\circ}\text{C}$  and their upper critical  
solution temperature (shown by U2)  $70^{\circ}\text{C}$  or higher. The  
5 lower critical solution temperatures is an important  
factor for practical purposes in the heat exchanger of a  
refrigerating apparatus, and the upper critical solution  
temperature is an important factor for practical  
purposes in a refrigerant compressor.

10 Fig. 9 is a diagram showing the structure of  
the refrigeration cycle of a refrigerating apparatus.  
The refrigerating apparatus comprising a refrigerant  
compressor 40, a condenser 41, a dryer 45, an expansion  
mechanism 42 and an evaporator 43 was operated by using  
15 each of the above-mentioned refrigerating machine oils  
together with flon 134a. Consequently, in the case of  
SUNISO 4GSD (a naphthenic mineral oil) and Z300A (an  
alkylbenzene oil) (trade names, mfd. by JAPAN SUN OIL  
Co., Ltd.), when the refrigerant was present in a large  
20 amount and lay idle in the compressor, a refrigerant  
layer having a high density and a refrigerating machine  
oil layer having a low density were present merely as a  
lower layer and an upper layer, respectively, owing to  
two-layer separation. Therefore, as shown in Fig. 7,  
25 i.e., the vertical cross-sectional view showing the  
principal part of a refrigerant compressor (an example  
of closed rotary compressor), oil supply to a shaft 4A,  
a main bearing 5 and a sub-bearing 6 is carried out by



1 suction of the refrigerant layer present merely as the  
lower layer through the suction opening 14 of a pump.  
The refrigerant layer has a lower viscosity than does  
the refrigerating machine oil. Therefore, when the  
5 refrigerant layer is supplied to the bearings, the  
resulting oil film is thin, so that contact between  
metal surfaces tends to occur. In addition, since the  
temperature of sliding frictional surfaces rises at  
once, the refrigerant was gasified, resulting in more  
10 severe conditions. When this phenomenon is repeated,  
damages due to scoring and seizing are caused in the  
shaft and the bearings, so that the performance  
characteristics of the refrigerant compressor are lost.

When the conventional refrigerating machine  
15 oil is used in the heat exchanger of the refrigerating  
apparatus shown in Fig. 9, for example, the evaporator  
43 used at 0° to -60°C, the refrigerating machine oil  
which has been discharged together with gas of the  
refrigerant from the compressor 40 undergoes two-layer  
20 separation in the evaporator 43 and adheres to the inner  
wall of the piping of the heat exchanger, and there is  
caused the residence of the refrigerating machine oil or  
the heat insulation of the heat exchanger. Therefore,  
the conventional refrigerating machine oils greatly  
25 deteriorate the cooling capability of the refrigerating  
apparatus and are of no practical use. In this point,  
the polyalkylene glycol listed as Conventional Example 3  
in Table 1 is advantageous because it has a lower



critical solution temperature of  $-60^{\circ}\text{C}$  and hence does not undergo two-layer separation in the evaporator 43. But, owing to its upper critical solution temperature of  $35^{\circ}\text{C}$ , it completely undergoes two-layer separation because the temperature of the compressor 40 during operation becomes at least  $80^{\circ}\text{C}$ . As in the case of Conventional Examples 1 and 2, when the polyalkylene glycol is supplied to the bearings, damages due to scoring and seizing are caused in the shaft and the bearing, so that the refrigerant compressor loses its performance characteristics.

In a refrigerant compressor having a hermetic motor, for example, the rotary compressor shown in Fig. 7, a refrigerating machine oil is, of course, required to have characteristics as an electrical insulating oil.

Fig. 2 shows the relationship between the water absorption and the volume resistivity of each of the ester oils according to the present invention and conventional mineral oil and polyalkylene glycol. Even in a condition in which the water content is controlled to be 500 ppm or less, the polyalkylene glycol as conventional example has a low volume resistivity of  $10^{12} \Omega\text{cm}$  or less owing to the ether linkages in the molecule and hence is not preferable.

On the other hand, the refrigerating machine oil having ester linkages introduced therein according to the present invention has a high volume resistivity (a high insulating capability) of  $10^{13} \Omega\text{cm}$  or more which



1 is in accordance with the standard value of electrical  
insulating oil prescribed in JIS C2320. Therefore, it  
can be sufficiently put to practical use. Although the  
mineral oil as conventional example has a high insulat-  
5 ing capability, it has a bad miscibility with flon 134a  
and cannot be put to practical use.

Next, the relationship among the kind,  
chemical structure and lower critical solution tempera-  
ture of ester oils suitable for flon 134a is explained  
10 below in detail with reference to Table 1.

The ester oil containing two or more ester  
groups in the molecule which is used in the present  
invention includes esters of monobasic or polybasic  
organic acids and polyhydric alcohols. Typical examples  
15 of the ester oil are hindered ester oils and complex  
ester oils which are represented by esters of neophentyl  
glycol, esters of trimethylolpropane or trimethyl-  
olethane, and esters of pentaerythritol. Table 1 shows  
the relationship amount the name, viscosity and critical  
20 solution temperatures of typical chemically synthesized  
products.

This Sheet Has Been Replaced



Table 1

|                      | Sample refrigerating machine oil |                                      | Viscosity (cSt)       |       | Critical solution temperature (°C) |           |     |
|----------------------|----------------------------------|--------------------------------------|-----------------------|-------|------------------------------------|-----------|-----|
|                      |                                  |                                      | 40°C                  | 100°C | U (upper)                          | L (lower) |     |
| Conventional Example | 1                                | Naphthenic mineral oil (SUNISO 4GSD) | 55.1                  | 5.9   | -                                  | >40       |     |
|                      | 2                                | Alkylbenzene oil (SUNISO Z300A)      | 60.1                  | 6.0   | -                                  | >40       |     |
|                      | 3                                | Propylene glycol monoether (PAG56)   | 54.0                  | 10.0  | 35                                 | -60       |     |
| Example              | 1                                | Note 1                               | NPG/n-C <sub>8</sub>  | 4.8   | 1.7                                |           | -29 |
|                      | 2                                |                                      | NPG/n-C <sub>7</sub>  | 2.8   | 1.2                                |           | -61 |
|                      | 3                                |                                      | NPG/2EH               | 7.0   | 2.1                                | >80       | -60 |
|                      | 4                                |                                      | NPG/i-C <sub>7</sub>  | 5.5   | 1.8                                | >80       | -70 |
|                      | 5                                |                                      | NPG/i-C <sub>11</sub> | 14.9  | 3.8                                | >80       | -40 |
|                      | 6                                | Note 2                               | TMP/n-C <sub>7</sub>  | 13.9  | 3.4                                |           | -20 |
|                      | 7                                |                                      | TMP/n-C <sub>6</sub>  | 10.8  | 2.8                                |           | -62 |
|                      | 8                                |                                      | TMP/i-C <sub>8</sub>  | 32.2  | 5.2                                |           | -27 |
|                      | 9                                |                                      | TMP/2EH               | 22.0  | 4.2                                |           | -33 |
|                      | 10                               |                                      | TMP/i-C <sub>7</sub>  | 14.9  | 3.4                                | >80       | -60 |
|                      | 11                               | Note 3                               | PET/n-C <sub>6</sub>  | 17.5  | 3.7                                |           | -44 |
|                      | 12                               |                                      | PET/2EH               | 52.0  | 6.7                                |           | -8  |
|                      | 13                               |                                      | PET/i-C <sub>7</sub>  | 28.0  | 4.8                                |           | -40 |
|                      |                                  |                                      |                       |       |                                    |           |     |

- Cont'd -

Table 1 (Cont'd)

|    |        |                           |      |     |     |      |
|----|--------|---------------------------|------|-----|-----|------|
| 14 | Note 4 | NPG/Glut/n-C <sub>6</sub> | 32.6 | 5.9 | >80 | <-75 |
| 15 |        | NPG/i-C <sub>7</sub> +    |      |     |     |      |
| 16 |        | AZP/NPG/n-C <sub>10</sub> | 29.5 | 5.0 | >80 | -45  |
| 17 |        | Glut/NPG/i-C <sub>6</sub> | 56.6 | 8.6 | >80 | -60  |

Note 1 NPG: esters of neopentyl glycol, i-C<sub>7</sub>:  $\text{CH}_3(\text{CH}_2)_3\overset{\text{CH}_3}{\underset{|}{\text{CH}}}\text{COOH}$ , n-C<sub>7</sub>:  $\text{CH}_3(\text{CH}_2)_5\text{COOH}$ ,  
i-C<sub>11</sub>:  $\text{CH}_3(\text{CH}_3)\text{CH}(\text{CH}_2)_7\text{COOH}$ .

Note 2 TMP: esters of trimethylolpropane, i-C<sub>8</sub>:  $\text{CH}_3-\overset{\text{CH}_3}{\underset{|}{\text{CH}}}-\overset{\text{CH}_3}{\underset{|}{\text{CH}}}\text{CH}_2\text{COOH}$ , n-C<sub>6</sub>:  $\text{CH}_3(\text{CH}_2)_4\text{COOH}$

Note 3 PTE: esters of pentaerythritol

Note 4 : complex esters, n-C<sub>10</sub>:  $\text{CH}_3(\text{CH}_2)_8\text{COOH}$ , i-C<sub>6</sub>:  $\text{CH}_3(\text{CH}_3)\text{CH}(\text{CH}_2)_2\text{COOH}$

1           Of the sample names in Table 1, the names of  
chemically synthesized ester oils are abbreviated. For  
example, in the case of NPG/n-C<sub>8</sub>, NPG is an abbreviation  
of neopentyl glycol, n-C<sub>8</sub> is an abbreviation of a normal  
5 organic acid (a straight-chain fatty acid) having 8  
carbon atoms, and NPG/n-C<sub>8</sub> denotes an ester of neopentyl  
glycol and the normal organic acid (the straight-chain  
fatty acid) having 8 carbon atoms. In the case of  
NPG/2EH, 2EH is an abbreviation of 2-ethylhexanoic acid  
10 and NPG/2EH denotes an ester of neopentyl glycol and 2-  
ethylhexanoic acid.

1)       As shown in Examples 1 to 4, the esters of  
neopentyl glycol (NPG) are esters of neopentyl glycol as  
dihydric alcohol and a monocarboxylic acid as monobasic  
15 organic acid, and are characterized by containing two  
ester groups in the molecule. Such a chemical structure  
has an important bearing on the miscibility with flon  
134a and the viscosity characteristics of the oils.

That is, ester oils of a monocarboxylic acid  
20 having 7 to 8 carbon atoms were satisfactory and had a  
lower critical solution temperature of -29°C to -70°C  
and a viscosity at 40°C of 2.8 to 7.0 cSt.

The smaller the number of carbon atoms of the  
monocarboxylic acid (the fatty acid), the lower the  
25 lower critical solution temperature. It was found that  
the lower critical solution temperature of the ester of  
2-ethylhexanoic acid (2EH) of Example 3 and the ester of  
isoheptanoic acid (i-C<sub>7</sub>) of Example 4 which have a



1 branched chain in the molecule is advantageously lower  
than that of the esters of Examples 1 and 2, respec-  
tively. The case of increasing the number of carbon  
atoms of the carboxylic acid to 11 for increasing the  
5 viscosity is Example 5. The ester of Example 5 was  
found to have a viscosity at 40°C of 14.9 cSt and a  
lower critical solution temperature of -40°C at the  
lowest.

2) Next, the esters of trimethylolpropanol (TMP)  
10 containing three ester linkages in the molecule are  
explained below with reference to Examples 6 to 10.

The ester oils obtained by the condensation of  
trimethylolpropane (TMP) as trihydric alcohol and a  
monocarboxylic acid as monobasic organic acid contain  
15 three ester groups in the molecule, and the mono-  
carboxylic acid has 6 to 8 carbon atoms. The ester oils  
have a viscosity at 40°C of 10.8 to 32.2 cSt and a lower  
critical solution temperature of -20°C to -60°C. Of  
these ester oils, ester oils having a lower critical  
20 solution temperature of -20°C or lower are the ester oil  
of heptanoic acid (n-C<sub>7</sub>) of Example 6, the ester oil of  
octanoic acid (n-C<sub>8</sub>) of Example 8 and the ester oil of  
2-ethylhexanoic acid (2EH) of Example 9. Ester oils  
having a lower critical solution temperature of -60°C or  
25 lower are the ester oil of hexanoic acid (n-C<sub>6</sub>) of  
Example 7 and the ester oil of isoheptanoic acid (i-C<sub>7</sub>)  
of Example 10. The ester oils of Examples 6 to 10 are  
also characterized in that the smaller the number of



1 carbon atoms, the lower the lower critical solution  
temperature, and that the lower critical solution  
temperature of the ester oils containing a branched  
chain is lower than that of the ester oils containing no  
5 branched chain even when the former ester oils and the  
latter ester oils have the same number of carbon atoms.

3) As shown in Examples 11 to 13, the ester oils  
obtained by the condensation of pentaerythritol (PET) as  
tetrahydric alcohol and a monocarboxylic acid contain 4  
10 ester groups in the molecule, and the monocarboxylic  
acid has 6 to 8 carbon atoms. The ester oils have a  
high viscosity at 40°C of 17.5 to 52.0 cSt and a lower  
critical solution temperature of -8°C to -44°C. Thus,  
the lower critical solution temperature is shifted to  
15 higher temperatures, as compared with the above-  
mentioned ester oils of dihydric alcohols and trihydric  
alcohols. Of the ester oils of Examples 11 to 13, ester  
oils having a lower critical solution temperature of  
-40°C or lower are the ester oil of hexanoic acid (n-C<sub>6</sub>)  
20 of Example 11 and the ester oil of isoheptanoic acid (i-  
C<sub>7</sub>) of Example 13. The ester oils of Examples 11 to 13  
are also characterized in that the smaller the number of  
carbon atoms, the lower the lower critical solution  
temperature, and that the lower critical solution  
25 temperature of the ester oils containing a branched  
chain is lower than that of the ester oil containing no  
branched chain.



1        4)        As a method for introducing 4 ester groups  
into the molecule, there is a method in which  
esterification is carried out by condensing a polyhydric  
alcohol and a monocarboxylic acid with a dicarboxylic  
5 acid (i.e. a typical dibasic organic acid) as the  
central constituent. By this method, the lower critical  
solution temperature can easily be lowered and the  
viscosity can easily be increased. Esters obtained by  
such a molecular design are complex esters and are  
10 explained with Examples 14 to 17 of the present  
invention.

Example 14 shows a complex ester of glutaric  
acid (abbreviated as Glut) as dicarboxylic acid,  
neopentyl glycol (NPG) as dihydric alcohol, and hexanoic  
15 acid (C<sub>6</sub>) as monocarboxylic acid. This complex ester  
had a viscosity at 40°C of 32.6 cSt, a viscosity at  
100°C of 5.9 cSt, and a lower critical solution  
temperature of -75°C or lower.

Example 15 shows the case where an ester  
20 having moderate viscosity grade was prepared by mixing  
the esters of Examples 4 and 16. This ester was also  
found to possess a lower critical solution temperature  
not much changed.

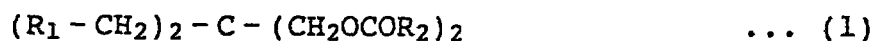
Example 16 shows a complex ester of adipic  
25 acid (abbreviated as AZP) as dicarboxylic acid,  
neopentyl glycol (NPG) as dihydric alcohol, and decanoic  
acid (n-C<sub>10</sub>) as monocarboxylic acid. Example 17 shows a  
complex ester of glutaric acid (Glut) as dicarboxylic



1 acid, neopentyl glycol (NPG) as dihydric alcohol, and  
 2 isohexanoic acid (i-C<sub>6</sub>) as monocarboxylic acid. These  
 3 complex esters were found to be so excellent that they  
 4 had a viscosity at 40°C of 54.5 to 56.6 cSt, a viscosity  
 5 at 100°C of 7.3 to 8.6 cSt, and a lower critical  
 6 solution temperature of -60°C. These results indicate  
 7 that a complex ester having a suitable viscosity can be  
 8 synthesized by determining properly the number of carbon  
 9 atoms (C<sub>2</sub> to C<sub>10</sub>) of a dicarboxylic acid as dibasic  
 10 organic acid and the number of carbon atoms (C<sub>5</sub> to C<sub>10</sub>)  
 11 of a monocarboxylic acid as monobasic acid, and  
 12 condensing the dicarboxylic acid, the monocarboxylic  
 13 acid, and a polyhydric alcohol in a properly chosen  
 14 molar ratio.

15 When these Examples are arranged, the esters  
 can be represented as follows by general formulas:

Esters of neopentyl glycol:



Esters of trimethylolalkane:

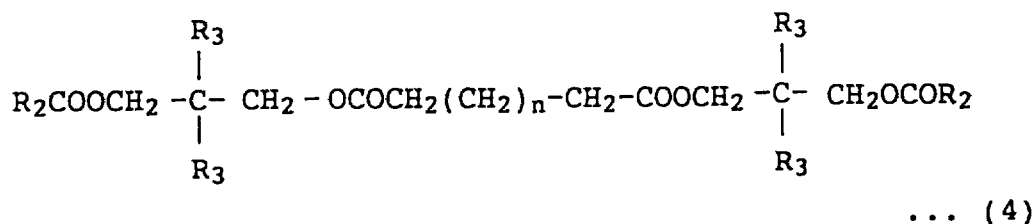


Esters of pentaerythritol:

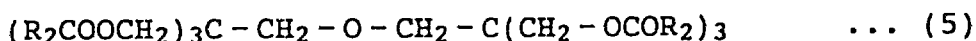


Complex esters:





1 In addition, examples of easily obtainable esters are esters of dipentaerythritol:



In the above formulas (1) to (5),  $\text{R}_1$  is H or an alkyl group having 1 to 3 carbon atoms,  $\text{R}_2$  is a  
5 straight-or branched-chain alkyl group having 5 to 12 carbon atoms,  $\text{R}_3$  is an alkyl group having 1 to 3 carbon atoms, and  $n$  is an integer of 0 to 5.

The viscosity could be optionally determined by choosing the kinds of the polyhydric alcohol and the  
10 carboxylic acid(s).

A moderate viscosity could easily be attained by blending a low-viscosity oil and a high-viscosity oil.

In the case of a refrigerating apparatus using  
15 a flon type refrigerant containing no chlorine, for example, flon 134a, a refrigerating machine oil capable of imparting fundamentally satisfactory performance characteristics and reliability to a compressor and the refrigerating apparatus can be obtained by selecting an  
20 oil having a lower critical solution temperature of  $0^\circ\text{C}$  or lower (the first target value) or an oil having a



- 1 lower critical solution temperature of  $-30^{\circ}\text{C}$  or lower  
(the second target value) both of which have a viscosity  
at  $40^{\circ}\text{C}$  of 2 to 70 cSt, preferably 5 to 32 cSt and a  
viscosity at  $100^{\circ}\text{C}$  of 1 to 9 cSt, preferably 2 to 6 cSt,  
5 from the hindered esters and the complex esters which  
contain two or more ester linkages in the molecule.

It was confirmed that these ester type  
refrigerating machine oils have a good miscibility not  
only with flon 134a but also with all flon type  
10 refrigerant gases containing no chlorine, for example,  
flon 152a (difluoroethane  $\text{CH}_3\text{CHF}_2$ ). The refrigerating  
machine oils were effective in imparting high  
performance characteristics and a high reliability to a  
refrigerating apparatus.

- 15 In addition, it was confirmed that since these  
ester oils according to the present invention are highly  
soluble also in conventional chlorine-containing flon  
type refrigerants (chlorofluorohydrocarbon type  
refrigerants) such as flon 12 and flon 22, they are  
20 effective also when used in part in admixture with these  
refrigerants.

However, since the conventional chlorine-  
containing flon type refrigerants are included in the  
list of compounds under regulation in use because of the  
25 problem of environmental disruption, it is preferable to  
adjust the proportion of the refrigerants to 50% or less  
and that of the ester oil according to the present  
invention to 50% or more.



1           Next, an example of refrigerating apparatus  
for achieving the second object of the present invention  
is given below.

Example 18

5           The rotary compressor shown in Fig. 7 which  
was a refrigerant compressor was incorporated into a  
refrigerating apparatus having the constitution shown in  
Fig. 9. At a compressor temperature of 100°C and a  
discharged gas pressure of 9.5 to 10 kgf/cm<sup>2</sup>G which were  
10 conditions of examining the reliability of a refrige-  
rator, a relationship between the viscosity of a  
refrigerating oil stored in the compressor and the  
coefficient of performance (COP), i.e., the ratio of the  
refrigerating capacity of the compressor to an input,  
15 was measured by using some of the ester oils with a  
typical viscosity grade exemplified in Table 1. The  
results obtained are shown in Fig. 3.

Fig. 3 shows a relationship between the actual  
viscosity of each refrigerating machine oil and the  
20 coefficient of performance (COP) which was determined  
for the ester oils according to the present invention  
having a viscosity at 40°C of 5 to 56 cSt and  
conventional examples, i.e., a polyalkylene glycol and  
an alkylbenzene oil (SUNISO Z-300A) used in combination  
25 with flon 12. In Fig. 3, the axis of abscissa refers to  
the actual viscosity of each refrigerating machine oil  
stored in the rotary compressor, and the axis of



1 ordinate to the coefficient of performance (expressed in  
terms of a relative value) of the compressor.

According to Fig. 3, when refrigerating  
machine oils are compared in the coefficient of  
5 performance by taking the coefficient of performance  
attained by the conventional combination of flon 12 and  
Z-300A (an alkylbenzene oil) having a viscosity at 40°C  
of 56 cSt, as 1.0, the coefficient of performance  
attained for the combination of the polyalkylene glycol  
10 (PAG56) of Conventional Example 3 and flon 134a is as  
small as 0.859, indicating that the energy efficiency is  
lowered by about 14%.

On the other hand, the complex ester according  
to the present invention with a viscosity at 40°C of  
15 56.6 cSt of Example 17 gave a satisfactory coefficient  
of performance of 0.906. It can be speculated that this  
result is attributable to a reducing effect on friction  
loss caused on the basis of the journal bearing theory  
represented by the theory of the formula (9), a reducing  
20 effect on oil-agitating power, a heat-dissipating  
effect, etc. which are brought about because the  
viscosity of the refrigerating machine oil which  
contains flon 134a dissolved therein becomes as low as  
4.35 cSt under the same operation conditions.

25 When the ester oils according to the present  
invention which had a still lower viscosity of 5 to 32  
cSt (at 40°C) were compared in the coefficient of



1 performance under the same conditions, the ester oil  
with a viscosity of 32.6 cSt (at 40°C) of Example 14,  
the ester oil with a viscosity of 14.9 cSt (at 40°C) of  
Example 5 and the ester oil with a viscosity of 14.9 cSt  
5 (at 40°C) of Example 10 gave coefficient values of  
0.926, 0.966 and 0.973, respectively. Thus, the  
coefficient of performance was increased in that order.  
On the other hand, in the case of the ester oil with a  
viscosity of 5.5 cSt (at 40°C) of Example 4, the  
10 coefficient of performance was 0.953, namely, it showed  
a tendency to be decreased a little.

From these results, it can be seen that an  
ideal ester oil suitable for the rotary compressor is an  
ester oil which has a viscosity at 40°C in the range of  
15 5 to 32 cSt (exactly, 5.5 to 32.6 cSt), i.e., a range  
around the most suitable value of 14.9 cSt, and contains  
two or more ester linkages in the molecule, as described  
above.

#### Example 19

20 Flon 134a and each of the refrigerating  
machine oils according to the present invention  
exemplified in Table 1 were used in a low-pressure  
vessel type reciprocating compressor, and the compressor  
was incorporated into a refrigerator, i.e., a  
25 refrigerating apparatus. The refrigerator was then  
subjected to a high-temperature reliability test



1 (pressure in case 1.6 kg/cm<sup>2</sup> abs, case temperature 85°C,  
100 V, 50 Hz).

Fig. 4 shows the test results. In this graph,  
the axis of abscissa refers to the measured value of  
5 viscosity of the refrigerating machine oil, and the axis  
of ordinate to the coefficient of performance (COP).  
The graph was obtained by plotting the coefficient of  
performance against the actual viscosity in actual  
operation of each of the sample refrigerating machine  
10 oils with a viscosity at 40°C of 5.5, 14.9, 22.0, 32.6  
and 56.6 cSt, respectively, shown in Examples in Table  
1. The coefficient of performance is in linear relation  
with the actual viscosity.

From the results shown in Fig. 4, it can be  
15 seen that the lower the viscosity of the refrigerating  
machine oil, the larger the coefficient of performance  
of the low-pressure vessel type reciprocating  
compressor. The refrigerating machine oils having an  
actual viscosity of 2 to 4.2 cSt and a viscosity at 40°C  
20 of 5.5 to 14.9 cSt can be said to be excellent. When  
the actual viscosity is less than 2 cSt, a decrease of  
the coefficient of performance and a lowering of the  
reliability of bearings tend to be caused because in the  
case of using a conventional material such as cast iron  
25 or an iron-based sintered material for producing the  
sliding parts of the compressor, the precision of  
finishing the surfaces of the sliding parts is limited,  
and therefore at too low an actual viscosity, the



1 lubrication on the surfaces gets into the so-called  
boundary lubrication region in which the contact between  
metal surfaces occurs.

#### Example 20

5           The lubrication in a refrigerating machine and  
a refrigerant compressor for achieving the third object  
of the present invention is explained below with  
reference to the following example.

For evaluating the lubrication, there were  
10 carried out a FALEX test in which a seizing load was  
measured in the air, and a high-pressure atmosphere  
friction test in which a seizing load was measured in a  
refrigerating machine oil containing 50% of flon 134a  
dissolved therein. Fig. 5 is a graph showing the  
15 correlation between the results of the two tests. The  
seizing load is as follows. An increasing load was  
applied to a rotating sample pin from both sides and a  
load at which seizing was caused was expressed in pound  
(lb).

20           In the present example, the ester oil of  
trimethylolpropane (TMP) and isoheptanoic acid (i-C<sub>7</sub>) of  
Example 10 exemplified in Table 1 was employed as a  
typical example of a refrigerating machine oil used in  
the refrigerating apparatus of the present invention,  
25 and there was determined a relationship between the kind  
and amount of an extreme pressure agent added to the  
ester oil and the lubricating characteristics. As to



1 materials for test pieces used for the evaluation of the  
lubrication, the materials for the pin and a block were  
standard materials, i.e., SNC-21 (nickel chrome steel)  
according to the standard of JIS and SUM 41 (resul-  
5 furized free-cutting steel) according to the standard of  
JIS, respectively. On the other hand, in the high-  
pressure atmosphere friction test, there was measured a  
load at which seizing was caused by friction between  
cylinders made of a material for shaft (eutectic  
10 graphite cast iron) and a material for roller (eutectic  
graphite cast iron tempered material), respectively,  
which had given satisfactory results in rotary  
compressors.

As shown in the case of sample No. 1 in Fig.  
15 5, the ester oil (the oil of Example 10) containing no  
extreme pressure agent gave a FALEX seizing load of 700  
lb and a seizing load of as low as 90 kgf/cm<sup>2</sup> in a flon  
134a atmosphere. On the other hand, in the case of  
sample No. 2 and sample No. 3, the FALEX seizing load  
20 was further increased by 400 lb to reach 1100 lb and the  
seizing load in a flon 134a atmosphere was increased by  
90 kg/cm<sup>2</sup> to reach 180 kg/cm<sup>2</sup>, owing to addition of each  
of the following extreme pressure agents. In the case  
of sample No. 2, CHELEX H-10 (a trade name, mfd. by  
25 SAKAI CHEMICAL INDUSTRY Co., Ltd.) which was an acidic  
phosphoric acid containing an active OH group in the  
molecule, was added in an amount of 1%. In the case of  
sample No. 3, an ester compound of an alkylene glycol



1 and phosphoric acid (butylpolyoxypropylene phosphate  
ester) was added in an amount of 1%.

That is, it was actually proved that the  
phosphorus-containing compounds such as the acidic  
5 phosphoric ester and the alkylene glycol phosphate ester  
compound act effectively as extreme pressure agents for  
preventing seizing, regardless of the presence of flon  
134a.

Next, a FALEX test was carried out  
10 continuously for a maximum time of 120 minutes while  
keeping an applied load constant at 100 lb, and the  
abrasion loss of a pin, i.e., an iron-based test piece,  
was measured. The results obtained are shown in Fig. 6.  
In the case of the oil of sample No. 4 which contained  
15 no extreme pressure agent, the pin was worn in an amount  
of 25 mg. On the other hand, in the case of both of the  
oils containing each of the above-mentioned phosphorus-  
containing compounds, the abrasion loss was as small as  
0.4 mg as shown for sample No. 7 and sample No. 8,  
20 namely, the abrasion loss could be reduced to one-fifth  
or less. The amount of the phosphorus-containing  
compound added is effective from about 0.05 wt% as shown  
for sample No. 5. The effect of the compound is  
increased with an increase of the amount. But when the  
25 amount exceeds 10 wt%, the improving effect on the  
lubrication hits the ceiling, so that the addition of  
the compound becomes economically disadvantageous and  
hence becomes impractical.



1           The abrasion loss could be reduced by  
increasing the viscosity of oil from 14.9 cSt (at 40°C)  
of sample No. 4 to 56.6 cSt (40°C) of sample No. 6.

          From the facts described above, it was found  
5   that the seizing load, abrasion resistance and lubrication of the iron-based sliding members could be greatly improved by adding a phosphorus-containing compound such as an acidic phosphoric ester, phosphoric ester, alkylene glycol phosphate ester or the like as an  
10 extreme pressure agent to the refrigerating machine oil used in the present invention, in an amount of 0.05 to 10 wt%, or by adjusting the viscosity of the oil to a high value instead of adding the extreme pressure agent. The refrigerating machine oil which contains the extreme  
15 pressure agent exhibits excellent performance characteristics particularly in the presence of a flon type refrigerant containing no chlorine, such as flon 134a.

#### Example 21

          An example for achieving the fourth object of  
20 the present invention is described below. The behaviors of electrical insulating materials used in the hermetic motor of a compressor, in the presence of both flon 134a and the refrigerating machine oil according to the present invention were evaluated. The results obtained  
25 are explained below with reference to Table 2 and Table 3.



1           Flon 134a and refrigerating machine oils were  
evaluated by observing the degree of deterioration of  
characteristics of a magnet wire (an enameled wire) and  
an insulating film material by a sealed tube test, for  
5 preventing external influence.

(1) Insulating characteristics of a magnet wire (an  
enameled wire)

As magnet wire test pieces, two kinds of test  
pieces, i.e., 5% elongated products and twisted-pair  
10 test pieces were subjected to a sealed tube test at  
150°C for 40 days. An explanation is given below with  
reference to the results shown in Table 2.

As a result of the sealed tube test carried  
out for a combination of flon 134a and the polyalkylene  
glycol listed as Conventional Example 3 in Table 1 which  
15 is a refrigerating machine oil said to be suitable for  
flon 134a, 5% elongated products of both the polyester  
wire (PEW) of sample No. 9 and the ester imide wire  
(EIW-R) of sample No. 10 in Table 2 were crazed, and the  
20 retention of the dielectric breakdown voltage of  
twisted-pair test pieces of these two kinds of wires was  
greatly lowered to 30 to 32%.

On the other hand, the same evaluation as  
above was carried out for a combination of flon 134a and  
25 the composite ester oil composed of glutaric acid  
(Glut), neopentyl glycol (NPG) and isohexanoic acid  
(i-C<sub>6</sub>) which is a refrigerating machine oil used in the  
present invention and is exemplified in Table 1.



1 Consequently, the same polyester wire (whose glass  
transition temperature is shown in Table 2) and  
polyester imide wire as the wires which were described  
above and deteriorated as conventional examples sample  
5 No. 9 and sample No 10, showed no abnormality in  
appearance, as shown for sample No. 11 and sample No.  
12. The retention of the dielectric breakdown voltage  
of these samples was as high as 95% or more, indicating  
that the degree of deterioration of the magnet wires was  
10 very low. The reason is as follows. The refrigerating  
machine oil according to the present invention has a low  
water content in the early stages and a high thermal  
stability, and hardly produce an acidic substance  
capable of accelerating hydrolysis, and these  
15 characteristics bring about the improving effects.

Sample No. 13 was obtained by coating the  
ester imide wire of sample No. 12 with a polyimide layer  
to form a composite. Sample No. 14 was a wire coated  
with a polyamide-imide alone (AIW). Both samples had  
20 satisfactory characteristics. It was found that such a  
magnet wire obtained by thus coating a layer with a high  
glass transition temperature on a layer with a low glass  
transition temperature contributes to the improvement of  
the reliability of a compressor because the upper coat-  
25 ing layer is effective as protective layer against an  
attack of flon 134a and the refrigerating machine oil.

(2) Insulating characteristics of insulating films

As a sealed tube test on insulating films for



1 motor, an insulating strength test at 130°C for 40 days  
was carried out, whereby the films were evaluated with  
respect to the appearance and the retention of tensile  
strength. The results obtained are shown in Table 3.

5 When a polyester film (Lumilar X<sub>10</sub>, a trade  
name, mfd. by Toray Industries, Inc.) conventionally  
used in the hermetic motor of a compressor was used in  
the conventional polyalkylene glycol oil shown for  
sample No. 15, its oligomer component was precipitated  
10 in the oil and the retention of tensile strength was  
83%.

On the other hand, in a combination of the  
complex ester oil of Example 17 according to the present  
invention and flon 134a, no oligomer was precipitated  
15 and the retention of tensile strength was as high as 89%  
or more in the case of all of Lumilar X<sub>10</sub> of sample No.  
16, PA-61M (a trade name, mfd. by Hitachi Kasei Co.,  
Ltd.), i.e., the polyamide-imide-coated polyester of  
sample No. 17, the polyphenylene sulfide (PPS) film of  
20 sample No. 18, and the polyether ether ketone (PEEK)  
film of sample No. 19. Thus, it was found that the  
electrical insulating system of a compressor using flon  
134a can be markedly improved in reliability.

That is, it was found that the insulation  
25 system of a hermetic motor can be completed by properly  
selecting a film from the group consisting of polyester  
films, polyamide-imide-coated polyester films, PPS films  
and PEEK films which have a glass transition temperature



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1 of 65°C or higher, and using the same in the presence of  
both flon 134a and the refrigerating machine oil con-  
taining two or more ester groups in the molecule accord-  
ing to the present invention. It was found that when  
5 the insulation system is thus completed, there can be  
solved the problem of precipitation of an oligomer  
component (the problem described above for the oil of  
Conventional Example 3 shown for sample No. 15), the  
problems in the performance characteristics of a  
10 compressor and a refrigerating apparatus which are  
caused by the lowering of the film strength, and the  
practical problems in the long-term reliability.



Table 2

| Sample No. | Insulation-coated winding wire                            | Glass transition temperature (°C)          | Results of evaluating performance characteristics with respect to resistance to an oil and flon 134a |                            |                                                    |
|------------|-----------------------------------------------------------|--------------------------------------------|------------------------------------------------------------------------------------------------------|----------------------------|----------------------------------------------------|
|            |                                                           |                                            | Oil tested                                                                                           | Appearance change (Note 1) | Retention of dielectric breakdown voltage (Note 2) |
| 9          | PEW (Polyester)                                           | 120-140                                    | Conventional Example 3                                                                               | Clazed                     | 30                                                 |
| 10         | EIW-R (Polyester imide)                                   | 190-210                                    | "                                                                                                    | "                          | 32                                                 |
| 11         | PEW (Polyester)                                           | 120-140                                    | Example 17                                                                                           | No abnormality             | 95                                                 |
| 12         | EIW-R                                                     | 190-210                                    | "                                                                                                    | No abnormality             | 98                                                 |
| 13         | RFW-V (Upper layer polyamide/lower layer polyester imide) | Lower layer 190-210<br>Upper layer 250-310 | "                                                                                                    | No abnormality             | 98                                                 |
| 14         | AIW (Polyamide imide)                                     | 250-310                                    | "                                                                                                    | No abnormality             | 98                                                 |

Sealed tube test: 150°C x 40 days

Note 1: 5% elongated wire

Note 2: A relative value obtained for a twisted pair test piece by dividing a value after the test by a value before the test (taken as 100).

Table 3

| Sample No. | Insulating film                           | Glass transition temperature (°C) | Results of evaluating performance characteristics with respect to resistance to an oil and flon 134a |                           |                                        |
|------------|-------------------------------------------|-----------------------------------|------------------------------------------------------------------------------------------------------|---------------------------|----------------------------------------|
|            |                                           |                                   | Oil tested                                                                                           | Appearance change         | Retention of tensile strength (Note 1) |
| 15         | Lumilar x 10 (polyester)                  | 65                                | Conventional Example 3                                                                               | Oligomer was precipitated | 89                                     |
| 16         | Lumilar x 10                              | 65                                | Example 17                                                                                           | None                      | 89                                     |
| 17         | PA-61M (Polyamide-imide-coated polyester) | 65                                | "                                                                                                    | None                      | 90                                     |
| 18         | PPS (Polyphenylene sulfide)               | 85                                | "                                                                                                    | None                      | 95                                     |
| 19         | PEEK (Polyether ether ketone)             | 143                               | "                                                                                                    | None                      | 98                                     |

Sealed tube test: 130°C x 40 days

Note 1: A relative value obtained by dividing a value after the test by a value before the test (taken as 100).

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1 Example 22

An example for achieving the fifth object of the present invention is described below.

It is known that particularly in refrigerating  
5 apparatus using a heat exchanger at 0°C or lower, the control of water content in the refrigerating apparatus has an important influence on the cooling capability and the assurance of the quality of an electrical insulating material. Therefore, the establishment of a technique  
10 for removing water is indispensable for the system of the refrigerating apparatus.

In a refrigeration cycle composed as shown in Fig. 9, flon 134a gas discharged from a compressor 40 is condensed into a liquid refrigerant by heat dispersion  
15 in a condenser 41. This high-temperature, high-pressure liquid refrigerant is transformed into low-temperature, low-pressure wet vapor by an expansion mechanism 42 and sent to an evaporator 43. In this series of steps, the water in the refrigerating apparatus is adsorbed and  
20 removed by a drying agent represented by synthetic zeolite in a dryer 45 provided between the condenser 41 and the expansion mechanism 42. It is important to choose the kind of the drying agent in consideration of a use environment in which the refrigerating machine oil  
25 according to the present invention and flon 134a coexist. The suitability of the drying agent is explained below with reference to Examples shown in Table 4.



1           Drying agents tested are synthetic zeolites  
having trade names of Molecular Sieves all manufactured  
by UNION SHOWA K.K. These synthetic zeolites are  
classified according to the adsorption capacity (%) at  
5   25°C and at a carbon dioxide gas partial pressure of 250  
mmHg which is used as an indication of the distribution  
of the diameter of pores for adsorption.

As to the suitability of the synthetic  
zeolites for flon 134a and the refrigerating machine oil  
10 according to the present invention, the results of a  
sealed tube test shown in Table 4 are explained below.

It was found that the synthetic zeollite  
composed mainly of sodium aluminate and sodium silicate  
shown as sample No. 20 (a conventional example; trade  
15 name 4ANRG) has a fluorine ion adsorption of as large as  
1.05%, so that problems due to the lowering of the  
strength or formation into powder are caused by the  
reaction of the synthetic zeolite. Sample No. 21 (a  
comparative example; trade name 4AXH-6) and sample No.  
20 22 (a comparative example; trade name XH-7) which are  
composed mainly of sodium aluminate, potassium  
aluminate, sodium silicate and potassium silicate have a  
carbon dioxide gas adsorption capacity of 4.5 to 1.5%  
and a reduced fuorine ion adsorption of 0.24%. But,  
25 they cannot put into practical use because their  
fluorine ion adsorption is still too large.

Sample No. 23 (an example; trade name XH-600)  
and sample No. 24 (an example; trade name XH-9) which



1 consist of a synthetic zeolite composed mainly of  
potassium aluminate, sodium aluminate, potassium  
silicate and sodium silicate have a carbon dioxide gas  
adsorption capacity of 0.2% and a greatly reduced  
5 fluorine adsorption of 0.04%. Since a fluorine ion  
adsorption which permits practical use is 0.1% or less,  
the value of 0.2% indicates that these samples are  
sufficiently usable.

The deterioration of characteristics of a  
10 synthetic zeolite itself by the adsorption of molecules  
of flon 134a is dependent on the distribution of pore  
diameter of the synthetic zeolite. It has been  
confirmed that for adjusting the fluorine ion adsorption  
to 0.1% or less, the employment of a synthetic zeolite  
15 whose carbon dioxide gas adsorption capacity has been  
adjusted to 1.0% or less is sufficient. That is, the  
following was found. When a synthetic zeolite composed  
of alkali metal silicates and alkali metal aluminates  
whose carbon dioxide gas adsorption at 25°C and at a  
20 carbon dioxide gas partial pressure of 250 mmHg has been  
adjusted to 1.0% or less, for example, Molecular Sieves  
XH-600 or XH-9 (trade names, mfd. by UNION SHOWA K.K.),  
is used as a drying agent in a refrigerating apparatus  
using flon 134a and the refrigerating machine oil  
25 containing two or more ester linkages in the molecule  
according to the present invention, which are placed  
together, only water can be effectively removed and  
fluorine ion adsorption hardly produce influences such



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- 1 as formation into powder or a lowering of the strength of beads, and therefore such a drying agent is very excellent for practical purposes.

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Table 4

| Sample No. | Drying agent<br>Name of sample | CO <sub>2</sub> adsorption capacity (%)<br>CO <sub>2</sub> partial pressure 250 mmHg (25°C) | Sealed tube test*                     |                             |
|------------|--------------------------------|---------------------------------------------------------------------------------------------|---------------------------------------|-----------------------------|
|            |                                |                                                                                             | Decomposition rate of refrigerant (%) | Fluorine ion adsorption (%) |
| 20         | 4ANRG                          | 12.0                                                                                        | 0.028                                 | 1.05                        |
| 21         | 4AXH-6                         | 4.5                                                                                         | 0.032                                 | 0.24                        |
| 22         | XH-7                           | 1.5                                                                                         | 0.035                                 | 0.24                        |
| 23         | XH-600                         | 0.2                                                                                         | 0.042                                 | 0.04                        |
| 24         | XH-9                           | 0.2                                                                                         | 0.04                                  | 0.04                        |

Sealed tube test: 150°C, 7 days

1           The carbon dioxide gas adsorption capacity at  
25°C and at a carbon dioxide gas partial pressure of 250  
mmHg should be 1.0% or less, and it is preferably as  
small as possible. When it is zero %, the drying agent  
5 absorbs water alone selectively but not fluorine ions,  
so that the drying agent becomes ideal molecular sieves.  
The present invention is constituted as explained above  
and hence has the following effects.

(1)           By using the refrigerating machine oil  
10 described below, in a refrigerating apparatus comprising  
a compressor, condenser, dryer, expansion mechanism and  
evaporator and using a flon type refrigerant containing  
no chlorine and having a critical temperature of 40°C or  
higher which is represented by flon 134a, the perform-  
15 ance characteristics and reliability of the compressor  
and the refrigerating apparatus can be markedly improved  
because the refrigerating machine oil and the refrige-  
rant are highly miscible with each other without their  
separation into two layers in the whole temperature  
20 range where the compressor and the refrigerating  
apparatus are used, and hence a lubricating oil film on  
the shaft and bearings of the compressor and the  
refrigerant-heat-transferring capability of a heat  
exchanger are assured. The refrigerating machine oil  
25 comprises as base oil an ester oil according to the  
present invention which contains two or more ester  
linkages in the molecule and has a refrigerating machine  
oil viscosity at 40°C of 2 to 70 cSt, preferably 5 to 32



1 cSt and a refrigerating machine oil viscosity at 100°C  
of 1 to 9 cSt, preferably 2 to 6 cSt. The refrigerating  
machine oil has a lower critical solution temperature of  
0°C or lower or -30°C or lower, and is used in the first  
5 target, i.e., a moderate-temperature refrigerating  
apparatus such as a dehumidifier, or the second target,  
i.e., a low-temperature refrigerating apparatus such as  
a refrigerator, respectively.

(2) Moreover, the performance characteristics and  
10 the reliability can be improved by an improving effect  
on the lubrication in the sliding portions of bearings  
of the refrigerant compressor which is obtained by  
adding a phosphoric ester type extreme pressure agent  
having OH groups in the molecule and other additives  
15 such as an abrasion-preventing agent, acid-capturing  
agent, antioxidant, defoaming agent, etc. to the above-  
mentioned refrigerating machine oil.

(3) By simultaneous use of the refrigerating  
machine oil containing two or more ester linkages in the  
20 molecule according to the present invention described  
below and flon 134a, the so-called performance characte-  
ristics can be improved, namely, the coefficient of  
performance indicating the performance characteristics  
of the compressor can be increased, the power consump-  
25 tion of the refrigerating apparatus using the compressor  
can be reduced, and the refrigerating capacity can be  
increased. In a high-pressure vessel type rotary  
compressor, the refrigerating machine oil is one which



1 has a viscosity at 40°C of 2 to 70 cSt, preferably 5 to  
32. In a low-pressure vessel type reciprocating  
compressor, the refrigerating machine oil is one which  
has a viscosity at 40°C of 2 to 70 cSt, preferably 5 to  
5 15 cSt.

(4) The electrical insulating performance and  
long-term reliability of the refrigerating apparatus can  
be markedly improved by using an insulation-coated  
winding wire with a glass transition temperature of  
10 120°C or higher and an insulating film with a glass  
transition temperature of 70°C or higher as insulating  
materials for a motor, and a refrigerating machine oil  
comprising as base oil the ester oil according to the  
present invention, in a refrigerant compressor using a  
15 flon type refrigerant containing no chlorine represented  
by flon 134a.

(5) By using a synthetic zeolite composed of  
alkali metal silicates and alkali metal aluminates  
having a carbon dioxide gas adsorption capacity at 25°C  
20 and at a carbon dioxide gas partial pressure of 250 mmHg  
of 1.0% or less, in the dryer constituting the  
refrigerating apparatus, water in the refrigeration  
cycle can be efficiently separated and adsorbed, and  
there can be prevented troubles caused by formation of  
25 the drying agent into powder by deterioration of the  
drying agent itself, namely, the problems caused by  
clogging of a piping for refrigerant with the drying  
agent and abnormal abrasion due to intrusion of the



- 1 drying agent into the sliding portions of the compres-  
sor. Therefore, the employment of the synthetic zeolite  
has a marked improving effect on the performance  
characteristics and the long-term reliability.
- 5 (6) The refrigerating apparatus having the  
constitution explained above can reduce the ozone  
depletion potential (ODP) and the global warming  
potential (GWP) which are in question in the terrestrial  
environment to zero and 0.3 or less, respectively,
- 10 relative to values attained when a conventional  
chlorine-containing flon type refrigerant gas (e.g. flon  
12) is used.



## WHAT IS CLAIMED IS:

1. A refrigerating apparatus comprising a refrigeration cycle comprising of at least a compressor, a condenser, a dryer, an expansion mechanism, and an evaporator, a refrigerant composed mainly of a fluoro-carbon type refrigerant containing no chlorine and having a critical temperature of 40°C or higher, and a refrigerating machine oil comprising as base oil an ester oil of one or more fatty acids which contains at

least two ester linkages ( $\text{-O-C-}$ ) in the molecule  
 $\begin{array}{c} \parallel \\ \text{O} \end{array}$

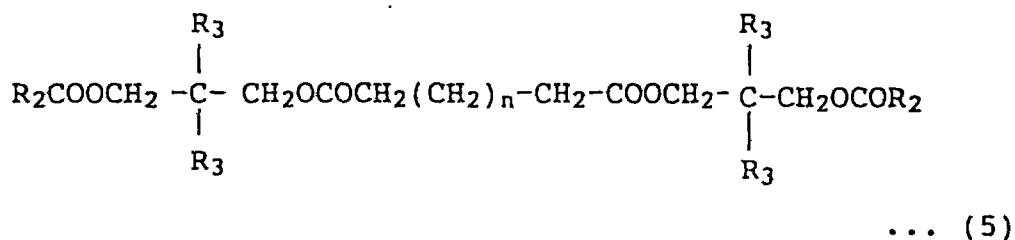
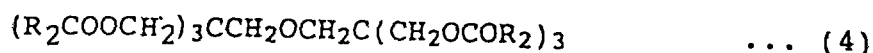
and has a viscosity at 40°C of 2 to 70 cSt and a viscosity at 100°C of 1 to 9 cSt.

2. A refrigerating apparatus according to Claim 1, wherein said ester oil comprises at least one member selected from the group consisting of the ester oils of one or more fatty acids which are represented by the following general formulas (1) to (5):



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wherein  $R_1$  is H of an alkyl group having 1 to 3 carbon atoms,  $R_2$  is a straight- or branched chain alkyl group having 5 to 12 carbon atoms,  $R_3$  is an alkyl group having 1 to 3 carbon atoms, and  $n$  is an integer of 0 to 5.

3. A refrigerating apparatus according to Claim 1 or 2, wherein said refrigerant composed mainly of a fluorocarbon type refrigerant containing no chlorine comprises at least one flon type refrigerant selected from the group consisting of fluorocarbons and hydrofluorocarbons.

4. A refrigerating apparatus according to Claim 3, wherein said flon type refrigerant comprises flon 134a.

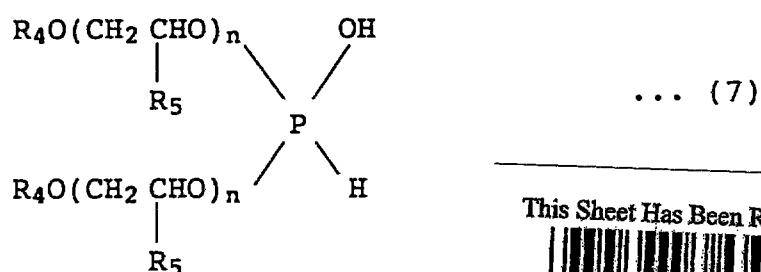
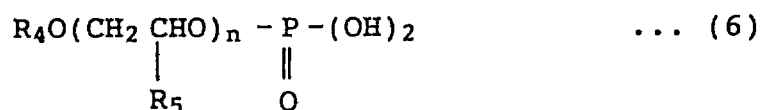
5. A refrigerating apparatus according to Claim 1, 2 or 4, wherein said refrigerating machine oil comprises at least 50 wt% of the above-mentioned ester oil as base oil.

6. A refrigerating apparatus according to Claim 1, 2 or 4, wherein an extreme pressure agent is added to said refrigerating machine oil.

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7. A refrigerating apparatus according to Claim 6, wherein as the extreme pressure agent, at least one member selected from the group consisting of alkylpolyoxyalkylene phosphate esters represented by the following formulas (6) and (7):



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(wherein  $\text{R}_4$  is an alkyl group having 1 to 8 carbon atoms, and  $\text{R}_5$  is H or an alkyl group having 1 to 3 carbon atoms; molecular weight 400 to 700) is added to the refrigerating machine oil in an amount of 0.05 to 10 wt%.

8. A refrigerating apparatus according to Claim 6, wherein as the extreme pressure agent, a dialkyl phosphate ester represented by the formula:



(wherein  $\text{R}_6$  is an alkyl group having 8 to 16 carbon atoms) is added to the refrigerating machine oil in an amount of 0.05 to 10 wt%.



9. A refrigerating apparatus according to any one of Claims 6 to 8, wherein at least one member selected from the group consisting of acid-capturing agents, antioxidants and defoaming agents is added to the refrigerating machine oil together with the above-mentioned extreme pressure agent.

10. A refrigerating apparatus according to any one of Claims 1 to 9, wherein a synthetic zeolite comprising a composite salt composed of alkali metal silicates and alkali metal aluminates which has a pore diameter of 3.3 angstrom or less and a carbon dioxide adsorption capacity at 25°C at a carbon dioxide gas partial pressure of 250 mmHg of 1.0% or less, is packed into the dryer as a drying agent.

11. A refrigerant compressor of high-pressure vessel type used in a refrigeration cycle which comprises a closed vessel stored with a refrigerating machine oil which accomodates a motor composed of a rotor and a stator, a rotating shaft fitted in the rotor, and a compressor section connected to the motor through the rotating shaft, and in which a high-pressure refrigerant gas discharged from the compressor section resides, said refrigerant being composed mainly of a flurocarbon type refrigerant containing no chlorine and having a critical temperature of 40°C or higher, and said refrigerating machine oil comprising as base oil an ester oil of one or more fatty acids which contains at



least two ester linkages  $\begin{pmatrix} -O-C- \\ \parallel \\ O \end{pmatrix}$  in the molecule

and has a viscosity at 40°C of 2 to 70 cSt and a viscosity at 100°C of 1 to 9 cSt.

12. A refrigerant compressor of low-pressure vessel type used in a refrigeration cycle which comprises a closed vessel stored with a refrigerating machine oil which accomodates a motor composed of a rotor and a stator, a rotating shaft fitted in the rotor, and a compressor section connected to the motor through the rotating shaft, and from which a high-pressure refrigerant gas discharged from the compressor section is directly exhausted, said refrigerant being composed mainly of fluorocarbon type refrigerant containing no chlorine and having a critical temperature of 40°C or higher, and said refrigerating machine oil comprising as base oil an ester oil of one or more fatty acids which contains at least two ester linkages

$\begin{pmatrix} -O-C- \\ \parallel \\ O \end{pmatrix}$  in the molecule and has a viscosity at 40°C

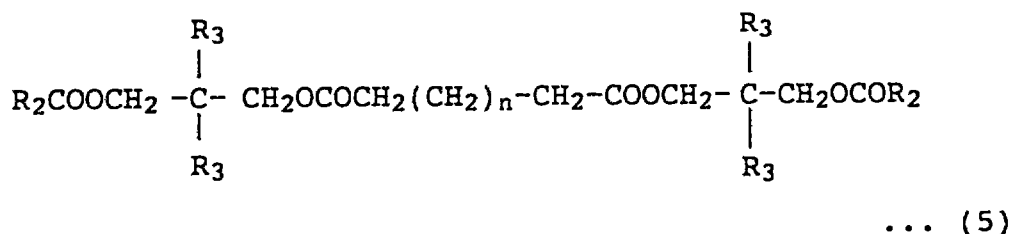
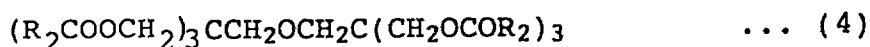
of 2 to 70 cSt and a viscosity at 100°C of 1 to 9 cSt.

13. A refrigerant compressor according to Claim 11 or 12, wherein said ester oil comprises at least one member selected from the group consisting of ester oils of one or more fatty acids which are represented by the following general formulas (1) to (5):



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wherein  $R_1$  is H or an alkyl group having 1 to 3 carbon atoms,  $R_2$  is an alkyl group having 5 to 12 carbon atoms,  $R_3$  is an alkyl group having 1 to 3 carbon atoms, and  $n$  is an integer of 0 to 5.

14. A refrigerant compressor according to Claim 11 or 12, wherein said refrigerant composed mainly of a fluorocarbon type refrigerant containing no chlorine comprises at least one flon type refrigerant selected from the group consisting of fluorocarbons and hydrofluorocarbons.

15. A refrigerant compressor according to Claim 14, wherein said flon type refrigerant comprises

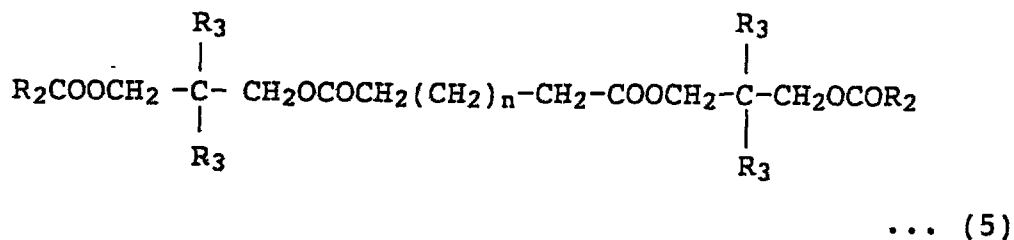
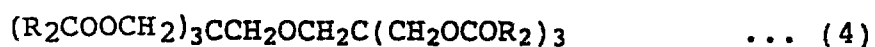


flon 134a.

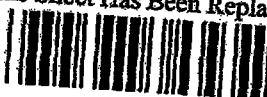
16. A refrigerant compressor according to Claim 11 or 12, wherein said refrigerant composed mainly of a fluorocarbon type refrigerant containing no chlorine is a refrigerant composed mainly of flon 134a, and said ester oil of one or more fatty acids which contains at

least two ester linkages  $(-O-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-)$  in the molecule

comprises at least one member selected from the group consisting of ester oils represented by the following general formulas (1) to (5):



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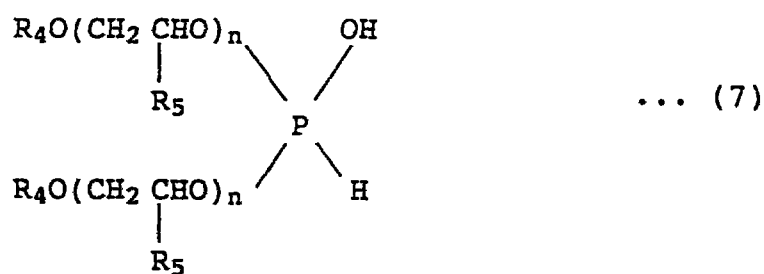
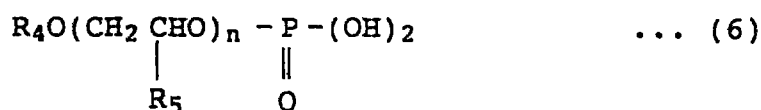


wherein  $R_1$  is H or an alkyl group having 1 to 3 carbon atoms,  $R_2$  is an alkyl group having 5 to 12 carbon atoms,  $R_3$  is an alkyl group having 1 to 3 carbon atoms, and  $n$  is an integer of 0 to 5.

17. A refrigerant compressor according to any one of Claims 11 to 16, wherein said refrigerating machine oil comprises at least 50 wt% of the above-mentioned ester oil as base oil.

18. A refrigerant compressor according to any one of Claims 11 to 17, wherein an extreme pressure agent is added to the refrigerating machine oil.

19. A refrigerant compressor according to Claim 18, wherein as the extreme pressure agent, at least one member selected from the group consisting of alkylpolyoxyalkylene phosphate esters represented by the following formulas (6) and (7):



(wherein  $R_4$  is an alkyl group having 1 to 8 carbon atoms, and  $R_5$  is H or an alkyl group having 1 to 3 carbon atoms; molecular weight 400 to 700) is added to the refrigerating machine oil in an amount of 0.05 to 10 wt%.



20. A refrigerant compressor according to Claim 18, wherein as the extreme pressure agent, a dialkyl phosphate ester represented by the formula:



(wherein  $\text{R}_6$  is an alkyl group having 8 to 16 carbon atoms) is added to the refrigerating machine oil in an amount of 0.05 to 10 wt%.

21. A refrigerant compressor according to any one of Claims 18 to 20, wherein at least one member selected from the group consisting of acid-capturing agents, antioxidants and defoaming agents is added to the refrigerating machine oil together with the extreme pressure agent.

22. A refrigerant compressor according to Claim 11 or 12 which comprises said closed-vessel accomodating a motor composed of a rotor and a stator, a rotating shaft, and a compressor section connected to the motor through the rotating shaft, wherein said winding wire of the stator comprises a core wire having an enamel coating having a glass transition temperature of 120°C or higher.

23. A refrigerant compressor according to Claim 22, wherein said enamel coating comprises at least one insulating layer selected from the group consisting of

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layers of polyester imides, polyamides and polyamide-imides.

24. A refrigerant compressor according to Claim 11 or 12, wherein the insulating film of the motor comprises a crystalline plastics film having a glass transition temperature of 50°C or higher.

25. A refrigerant compressor according to Claim 24, wherein said insulating film of the motor comprises at least one insulating film selected from the group consisting of films of polyethylene terephthalates, polybutylene terephthalates, polyphenylene sulfides, polyether ether ketones, polyethylene naphthalates, polyamide-imides, and polyimides.



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