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(71) Applicant: **Hitachi Home & Life Solutions, Inc.,**
Minato-ku,
Tokyo 105-8410 (JP)

(72) Inventors:
- **Ohta, Ryo**
c/o Hitachi, Ltd.
Chiyoda-ku
Tokyo 100-8220 (JP)
- **Nakakawaji, Takayuki**
c/o Hitachi, Ltd.
Chiyoda-ku
Tokyo 100-8220 (JP)
- **Gommori, Masahiko**
Hitachi Home&Life Solutions Inc.
Tochigi 329-4493 (JP)
- **Kouno, Takeshi**
c/o Hitachi, Ltd.
Chiyoda-ku
Tokyo 100-8220 (JP)

(74) Representative: **Beetz & Partner**
Patentanwälte,
Steinsdorfstrasse 10
80538 München (DE)

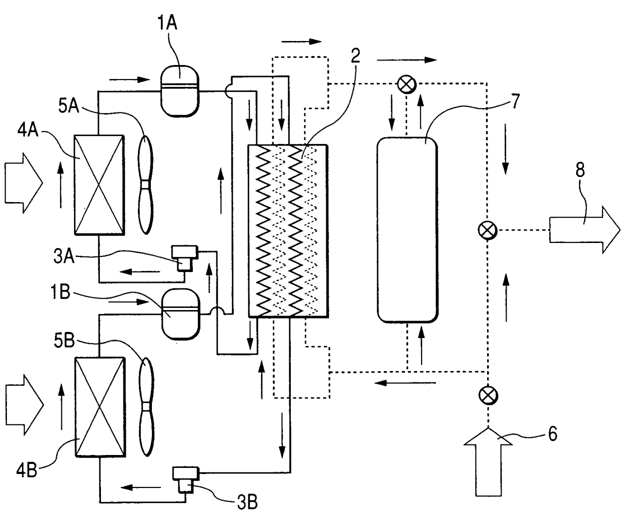
(54) **Heat-pump hot-water boiler having a refrigeration cycle and refrigeration oil therefor**

(57) The invention relates to heat-pump hot-water boilers wherein carbon dioxide is used as refrigerant, and particularly to a refrigeration oil which is capable of avoiding mechanical damages to enclosed-type motor-driven compressors and suppressing electrical leak currents under the regulated permissible value.

The refrigeration oil is a mixture of an oil being highly compatible with carbon dioxide and an oil being less compatible with carbon dioxide and has a dielectric constant of up to 3.0.

The refrigeration oil is composed of a poly-α-olefin oil and/or a mineral oil and a polyol ester oil which is preferably a sterically hindered ester of a polyhydric alcohol with one or more monohydric fatty acids.

FIG. 1



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Description

BACKGROUND OF THE INVENTION

[0001] This invention relates to heat-pump hot-water boilers and specifically to the technology of refrigeration oil for enclosed type motor driven compressors having a refrigeration cycle using carbon dioxide as refrigerant.

[0002] Recently, carbon dioxide (CO_2) which is one of natural refrigerants has got a lot of attention as a refrigerant for refrigeration cycles because it is good for the protection of the global environment and possesses incombustibility and low toxicity. Carbon dioxide can be used as a refrigerant in heat-pump hot-water boilers, electric car air conditioners, heaters for cold districts, automatic vending machines, and other products.

[0003] Further, for the protection of the global environment, there is the demand that these products save energy and work more efficiently. For this purpose, recent heat-pump hot-water boilers use the carbon dioxide refrigerant. Such a hot-water boiler produces about one fifth of the running costs of a general gas type hot-water heater for home use, and its efficiency is 3.0 times or more (in the coefficient of performance) higher than that of general electric water heaters. When a hydro-fluoro carbon (HFC) refrigerant is used, water cannot be heated up to about 60 °C because of the thermal physicality of the refrigerant, and in hot-water boilers using an HFC refrigerant a compressor of higher output must be used. Contrarily, hot-water boilers using a CO_2 refrigerant can produce hot water of about 90 °C because of the thermal physicality of that refrigerant.

[0004] The hot-water supplying methods of heat-pump hot-water boilers are grouped into two. One method is running the heat-pump cycle using late-night electric power and storing the hot water for 1-day domestic use in a tank. The other method is an instantaneous water heater which runs the heat-pump cycle to supply a required quantity of hot water every time when hot water is used. The instantaneous water heater requires an auxiliary small water tank to supply hot water before the heat-pump cycle is ready to supply hot water.

[0005] Generally, a hot-water storage system is prevailing, but the tank must be greater since the quantity of hot water to be used is dependent upon the capacity of the storage tank. Consequently, such a great tank cannot be housed in the heat-pump cycle unit and must be accommodated in an additional storage tank unit. This makes the boiler wider (in installation space) and heavier (in weight).

[0006] Meanwhile, although the instantaneous water heater requires a high-output compressor, the instantaneous water heater can supply hot water without breaking up the supply of hot water every time hot water is required. The auxiliary storage tank of the instantaneous water heater need not be so big. It can be of a very small capacity. Therefore, the tank can be housed in the heat-pump cycle unit. This can reduce the installation space and the weight of the instantaneous water heater. Therefore, the water heater can be placed in a narrow space like rooms in multiple dwelling houses like a condominium. Further, since the running time of the instantaneous water heater becomes much shorter than that of the hot-water storing boiler, the instantaneous water heater can improve the COP and save more energy.

[0007] By the way, a refrigeration oil for the compressor of the refrigeration cycle is generally included in the refrigerant for lubrication, sealing, and cooling of the sliding part. However, the compressor of the refrigeration cycle using a carbon dioxide refrigerant is run under very severe compressing conditions of high temperature (120 to 130 °C) and high pressure (approx. 15 MPa). For assurance of reliability of the compressor, the refrigeration oil is demanded to be highly lubricant, energy-saving, and highly efficient. Since the motor-driven compressor uses mainly heat-resistant PET (polyethylene terephthalate) as the insulating material by which carbon dioxide produces hydrogen carbonate ions and protons in the presence of lots of water in the system, the refrigeration system may be more deteriorated by the CO_2 refrigerant than the HFC refrigerant. Therefore, the water absorbing property of the refrigeration oil should preferably be low.

[0008] As disclosed in the Japanese laid-open patent application Hei 10-46169 (Patent Document 1), a heat-pump hot-water boiler using carbon dioxide as the refrigerant mainly adopts, as the refrigeration oil, polyalkylene glycol oil whose both ends are alkylated because it has a good compatibility with the refrigerant and thermochemical stability. However, the volume resistivity of the polyalkylene glycol oil as the electric insulating oil is much lower than the standard (10^{13} Ω·cm) and its dielectric constant ε (ε = approx. 5.0) is extremely high. Therefore, when running, the motor-driven compressor leaks current more than a permissible leak value (1.0 mA or less) regulated by Electrical Appliance and Material Safety Law. This is a problem.

[0009] The purposes of Electrical Appliance and Material Safety Law are to control production, import, and distribution of electric appliances and materials, promote private business units to perform independent actions to assure safety of electrical appliances and materials, and prevent dangers and problems of electrical appliances and materials.

[0010] It is known that a current leaking from the motor-driven compressor increases in proportion to the speed of the motor. Therefore, the leak current becomes very high when a high-capacity motor-driven compressor is started at a high speed in the same manner that the instantaneous heat-pump boiler is started. Further, since the polyalkylene glycol oil is highly water-absorbent, it requires time and facility to control the water content in the oil. Although the polyalkylene glycol oil is stable against hydrolysis, water in the oil will hydrolyze the ester-based insulating film in the motor-driven compressor and deteriorate the insulating characteristics of the insulating film.

[0011] Meanwhile, the Japanese laid-open patent application JP 2000-104084 (Patent Document 2) discloses a polyol ester oil as a refrigeration oil which is compatible with carbon dioxide excluding the polyalkylene glycol oil. However, the polyol ester oil is too high in compatibility with the carbon dioxide refrigerant. This means that the solution viscosity drops extremely, that the viscosity of the oil to be added also becomes very high, that the sealing ability of the compressor sections goes down, and that the compression efficiency will not be improved. Particularly, since the heat pump cycle using a carbon dioxide refrigerant is run in a supercritical status, the refrigeration oil will leak from the compressor and run through the refrigeration cycle if its compatibility is too high. This will increase a pressure loss and reduce the heat-exchange efficiency drastically.

[0012] Contrarily, the Japanese laid-open patent applications JP 2001-294886 (Patent Document 3) and JP 2000-110725 (Patent Document 4) disclose the use of hydrocarbon oils which are good in electric characteristics such as dielectric constant, low in water absorbing property, and non-compatible with carbon dioxide. However, the hydrocarbon oils are less lubricative and cannot be used under severe compressing conditions when carbon dioxide is used as refrigerant. A poly-α-olefin oil which is a kind of hydrocarbon oil has a high viscosity index and high flowability at low temperature, but the quantity of oil to be returned to the compressor becomes less. Similarly, an alkylbenzene oil is not preferable because its viscosity index is low, and the oil becomes very viscous in the low-temperature section in the refrigeration cycle and is apt to stay there.

SUMMARY OF THE INVENTION

[0013] Basically it is preferable to use a hydrocarbon oil such as poly-α-olefin oil and a mineral oil which never or hardly dissolves into carbon dioxide (having non-compatibility with carbon dioxide) as disclosed in the Patent Documents 3 and 4 as a refrigeration oil for a heat-pump type hot water boiler since the hydrocarbon oils are good in sealing the sliding section of the compressor and increase the efficiency of compression. Further, since the hydrocarbon oils are low in dielectric constant and water-absorbing property, the hydrocarbon oils will not cause problems such as increase of leak currents and deterioration of insulating materials.

[0014] Although the hydrocarbon oils never or hardly dissolve into carbon dioxide, however, they become more fluid at high temperatures at which the compressor runs critically, leak together with the refrigerant from the compressor into the refrigeration cycle, and keep on circulating through the refrigeration cycle. When the circulating refrigeration oil reaches the cold section of the refrigeration cycle, it becomes less fluid and stagnates there. As the result, the quantity of refrigeration oil returned to the compressor gradually goes down and finally, there is left no oil in the sliding section of the compressor, causing the sliding section to be abraded or burnt in. By the way, a poly-α-olefin oil has a high viscosity index and high flowability at low temperature, but the quantity of oil to be returned to the compressor is not always assured.

[0015] Therefore, the refrigeration oil must be compatible with carbon dioxide to assure that the required quantity of oil is returned to the compressor. However, since the polyalkylene glycol oil which is compatible with carbon dioxide has an extremely high electric characteristic (e.g. dielectric constant), the current leaking from the running of the motor-driven compressor goes over the regulated permissible leak value. Since the polyalkylene glycol oil is highly water-absorbent, it deteriorates the insulating characteristics of the motor-driven compressor. In other words, any water content in the refrigeration cycle will hydrolyze the carbon dioxide refrigerant into carbonic acid which greatly reduces the mechanical strength and elongation of the ester-based insulating film.

[0016] Furthermore, the polyol ester oil compatible with carbon dioxide is too compatible with the carbon dioxide refrigerant. When used by the heat pump cycle using a carbon dioxide refrigerant in a supercritical status, the refrigeration oil will leak from the compressor and run through the refrigeration cycle since its compatibility is too high. This will increase a pressure loss and reduce the heat-exchange efficiency drastically.

[0017] An object of this invention is to assure that the necessary quantity of refrigeration oil is returned to a motor-driven compressor which uses a carbon dioxide refrigerant and to suppress the current leak from the motor-driven compressor under the permissible value.

[0018] To accomplish the above object, this invention teaches to use a refrigeration oil which is a mixture of multiple oils to control the dielectric constant to be up to 3.0 for the enclosed type motor-driven compressor.

[0019] In accordance therewith, the above problem is solved according to the independent claims. The dependent claims relate to preferred embodiments of the concept o the present invention.

[0020] The present invention pertains to heat-pump hot-water boilers having a refrigeration cycle operated with carbon dioxide as refrigerant wherein specific refrigeration oils are used.

[0021] The invention further relates to refrigeration oils suitable for compressors; in particular for refrigerators, air conditioning systems and heat-pumps, such as heat-pump hot-water boiler or heating systems.

[0022] Basically, a refrigeration oil having a proper compatibility with carbon dioxide is preferable to assure the quantity of refrigeration oil returned to the motor-driven compressor which compresses a carbon dioxide refrigerant. This invention has been invented noticing the properties of CO_2-compatible and CO_2-non-compatible refrigeration oils which are opposite to each other that a CO_2-compatible refrigeration oil which excels in assurance of the quantity of refrigeration oil returned to the compressor has a high dielectric constant and increases a leak current, but that a CO_2-non-compatible refrigeration oil which never or hardly dissolves into carbon dioxide less excels in assurance of the quantity of returned refrigeration oil has a low dielectric constant and suppresses a leak current.

[0023] In other words, it is possible to prepare a refrigeration oil which has a proper compatibility with carbon dioxide by mixing multiple oils to have a dielectric constant of up to 3.0. This refrigeration oil can solve the oil return problem that the oil return property is not assured when a non-compatible refrigeration oil is used singly, prevent the sliding section of the compressor from being worn out, and suppress the leak current from the motor-driven compressor under the regulated permissible value, solving the problem which occurs when a CO_2 non-compatible refrigeration oil is used singly.

[0024] In this case, the refrigeration oil which has a proper compatibility with carbon dioxide means a refrigeration oil which has a high viscosity index and a high flowability at low temperature to assure the quantity of refrigeration oil returned to the compressor. The dielectric constant of the refrigeration oil is measured by a method standardized by JIS C-2101.

[0025] Accordingly, it is preferable to mix at least an oil which is highly compatible with CO_2 and an oil which is not so compatible with CO_2. For example, the oil which is highly compatible with CO_2 is a polyol ester oil, and the oil which is not so compatible with CO_2 is preferable to select from one of a poly-α-olefin oil and a mineral oil. And a naphthene-based mineral oil or a paraffin-based mineral oil can be used as the mineral oil.

[0026] In this case, the content of the polyol ester in the mixture should be 5 to 70 % by weight and the remaining part should be at least one of a poly-α-olefin oil and a mineral oil excluding general additives such as a lubrication improver and an antioxidant. More preferably, the content of the polyol ester in the mixture should be 5 to 30 % by weight. If the content of the polyol ester in the mixture is less than 5 % by weight, the quantity of the oil will not be returned sufficiently to the compressor and the lubricating property of the mixture oil is not sufficient. As the result, the sliding section of the compressor will be worn out.

[0027] If the content of the polyol ester in the mixture exceeds 70 % by weight, the refrigeration oil will move into the refrigeration cycle. This may cause a great pressure loss and a great reduction in heat exchange efficiency. Furthermore, the polyol ester oil has a water-absorbing property. It is not easy to control the water content in the oil, and the water in the oil will hydrolyze and deteriorate the oil.

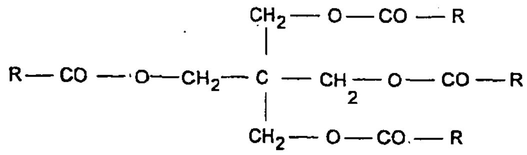
[0028] The refrigeration oil which is a mixture of a polyol ester oil and at least one of a poly-α-olefin oil and a mineral oil should preferably have a kinematic viscosity of 5 to 15 mm^2/s at 100 °C and a viscosity index of 100 or more. In other words, since the refrigeration oil of this invention can greatly allow carbon dioxide to permeate the oil, the refrigeration oil should preferably be a little more viscous than the chlorofluorocarbon-based refrigeration oil from the point of view of sealing. Specifically, the viscosity of the refrigeration oil for a rotary type refrigerant compressor should preferably be 2 to 8 mm^2/s at 100 °C and that of a scroll type compressor should preferably be 7 to 15 mm^2/s at 100 °C.

[0029] In other words, if the kinetic viscosity is less than the above value at 100 °C, the compressor cannot fully keep the abrasion resistance and the sealing ability and may reduce the compression efficiency. Further, if the kinematic viscosity at 100 °C exceeds the above value, the viscous resistance and the mechanical loss go up. This reduces the compression efficiency. Furthermore, the refrigeration oil becomes more viscous and the quantity of return oil may become less. The viscosity of the refrigeration oil is measured by a method standardized by JIS K-2283.

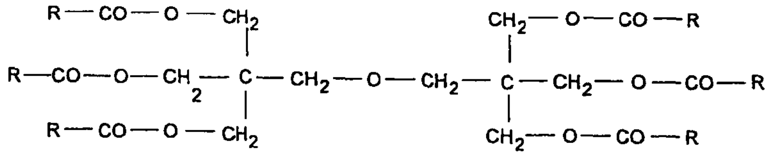
[0030] To prevent stagnation of the refrigeration oil in the cold part of the refrigeration cycle, the viscosity index of the refrigeration oil of this invention should preferably be 100 or more at which the return of the refrigeration oil to the compressor can be assured. The refrigeration oil of this invention can contain any of general additives such as lubrication improver, antioxidant, acid capture, defoamer, and metal inactivator. The refrigeration oil will not be affected by these additives at all.

[0031] Although the poly-α-olefin oil has a molecular distribution, the poly-α-olefin oil should preferably contain 50 % by weight of components which have 20 to 50 carbon atoms per molecule. If the poly-α-olefin oil contains a lot of components which have 20 or less carbon atoms per molecule, the carbon dioxide refrigerant which is highly compressed and in a critical status will easily leak out from the compressor. Contrarily, if the poly-α-olefin oil contains a lot of components which have 50 or more carbon atoms per molecule, its flowability drastically drops at low temperature.

[0032] A preferable polyol ester oil is a sterically hindered and thermally stable polyol ester oil which is prepared from a polyhydric alcohol and a monohydric fatty acid. For example, representative polyhydric alcohols are pentaerythritol and di-pentaerythritol. Monohydric fatty acids are pentanoic acid, hexanoic acid, heptanoic acid, octanoic acid, 2-methylbutanoic acid, 2-methylpentanoic acid, 2-methylhexanoic acid, 2-ethylhexanoic acid, isooctanoic acid, and 3,5,5-trimethylhexanoic acid. These fatty acids are used singly or in combination. Particularly, the base oil of the refrigeration oil should preferably be at least one selected from the group of fatty ester oils having at least four ester bonds in each molecule which are expressed by formula (1) and/or (2):



(1),



(2),

wherein R, which may be the same or different, is a linear or branched-chain alkyl group of 4 to 11 carbon atoms.

[0033] Mineral oils available are naphthene-based mineral oils and paraffin-based mineral oils. For example, they are burning oils obtained by normally purifying a distillate which is obtained by distilling paraffin-group crude oil, intermediate group crude oil, or naphthene-group crude oil at atmospheric pressure, or distilling the residue of atmospheric distillation at reduced pressure; deep-dewaxed oils obtained by deep-dewaxing the purified oils, and hydrogenated oils obtained by hydrogenating oils. Various purifying methods are available for the above.

[0034] The refrigeration oil of this invention can assure that a sufficient quantity of refrigeration oil is returned to a motor-driven compressor which absorbs and compresses a carbon dioxide refrigerant, and reduce the current leak of the motor-driven compressor under the permissible value.

BRIEF DESCRIPTION OF THE DRAWINGS

[0035]

Fig. 1 is the basic system configuration of a heat-pump hot-water boiler of an embodiment of this invention.
Fig. 2 is a layout of major units of the embodiment shown in Fig. 1.
Fig. 3 is a longitudinal sectional view of an enclosed type motor driven compressor as an embodiment of a horizontal scroll type compressor to which the invention can be applied.

DETAILED DESCRIPTION OF THE INVENTION

[0036] This invention will be more clearly described with reference to the following embodiments. Although the description refers to embodiments applied to a heat-pump hot-water boiler (hereinafter simply termed a boiler) which uses carbon dioxide as a refrigerant, this invention is not limited to this. This invention can be also applied to electric car air conditioners, heaters for cold districts, automatic vending machines, and other products.

[0037] Fig. 1 shows the basic system configuration of a boiler which is an embodiment of this invention. Fig. 2 shows the layout of major units of this embodiment. As shown in Fig. 1, the boiler of this embodiment has two cycles: a refrigerant cycle (indicated by solid lines) in which circulates a carbon dioxide refrigerant, and a water-heating cycle (which is indicated by dotted lines). The boiler of this embodiment is of an instantaneous type which runs a heat-pump cycle to supply a required quantity of hot water every time when hot water is used. However, this invention is not limited to this type. However, since the instantaneous type boiler must be equipped with a high-power compressor, its leak current and abrasion of the compressor are not negligible. Although the instantaneous type boiler of this embodiment contains two refrigeration cycles for high output, this invention is not limited to this.

[0038] First will be explained the carbon dioxide refrigerant cycle. The compressors 1A and 1B compress a refrigerant gas of low temperature and low pressure and send the compressed refrigerant gas of high temperature and high pressure to the water-refrigerant heat exchanger 2. In the heat exchanger 2, the heat is sensibly transferred from the refrigerant gas to water of low temperature. The cooled refrigerant gas turns to the refrigerant of low temperature and low pressure through the motor-driven expansion valves 3A and 3B and sent to the air heat exchangers 4A and 4B.

[0039] In the air heat exchangers 4A and 4B, the refrigerant absorbs heat from the ambient air and vaporizes. The cooled air is blown away by fans 5A and 5B. The refrigerant gas of low temperature and low pressure sent from the air heat exchanger 4A and 4B returns to the compressors 1A and 1B. This cycle is repeated. This type of boiler using carbon dioxide as the refrigerant can easily produce hot water of almost 100 °C since the carbon dioxide refrigerant exceeds the high critical point in the supercritical cycle and a desired pressure can be set.

[0040] Next will be explained the water heating cycle. Water of low temperature fed from the water supply port 6 is sent to water refrigerant heat exchanger 2, heated by the refrigerant into hot water, stored in the hot water tank 7, and then served through the taphole 8. In serving of hot water, the hot water from heat exchanger 2 is mixed with cool water fed from the water supply port 6 to control the temperature of hot water before being serviced. The heat exchanger 2 is also used to heat up hot water in the hot water tank 7, water in a bath tub (not shown in the figure), and so on. The heat exchanger 2 is also used as a heat source for a home total energy system including floor heating system and bathroom heating system.

[0041] The instantaneous water heater of this invention can have only a small auxiliary tank as the hot water tank 7 although a general heat-pump hot-water boiler must have a large-capacity hot water tank and provide separate cabinets to house a heat source tank unit and a hot water tank unit. Therefore, the instantaneous water heater can house a heat source tank unit and a hot water tank unit together in a single cabinet as shown in Fig. 2. This can save installation space dramatically.

[0042] The compressors 1A and 1B are usually scroll or rotary displacement type compressors. Fig. 3 shows a longitudinal sectional view of an enclosed type motor-driven compressor of a horizontal scroll type as an example. As shown in the figure, the compression mechanism of the compressor 1A or 1B comprising of the spiral lap 11 perpendicular to the end plate 10 of the stationary scroll member 9, the rotating scroll member 14 made of the end plate 12 and the lap 13 which are substantially the same as those of the stationary scroll member 9, wherein these members are engaged with each other with the laps 11 and 13 are faced to each other.

[0043] When the rotating scroll member 14 is turned by the crank shaft 15, the outermost one of the compression chambers 15a, 15b, and so on which are formed by the stationary and rotating scroll members 9 and 14 moves towards the center of the scroll members 9 and 14 while reducing the volume gradually as the rotation proceeds. When reaching the centers of the scroll members 9 and 14 and the vicinities, the compression chambers 15a, 15b, and so on communicate with the discharge port 16 and discharge the compressed gas from the compression chambers to the outside through the discharge pipe 17.

[0044] The compressor of Fig. 3 has electric motor 19 in the pressure vessel 18 and is driven to compress by the crank shaft 15 which rotates at a constant speed or a speed corresponding to a voltage controlled by an inverter (not shown in the figure). An oil pool is provided below the discharge pipe 17. Refrigeration oil 20 in the pool is supplied for lubrication by a pressure difference through the oil hole 21 in the crank shaft 15 to the sliding section at which the rotating scroll member 14 and crank shaft 15 slide and the bearing 22 and so on.

[0045] Below will be explained examples of refrigeration oils used by compressors 1A and 1B of a boiler which uses carbon dioxide as the refrigerant in accordance with the above embodiment.

(Embodiment 1)

[0046] The embodiment 1 actually ran the boiler of Fig. 1 for 2160 hours. In this actual service test, the boiler is operated in a temperature-controlled room which is kept at 20 °C in a summer temperature condition, and supply hot water of 60 °C which is a hot water storage condition.

[0047] Table 1 is a list to show various kinds of refrigeration oil components which are compound A (PAO), compound B (POE), and other compounds which are used to the embodiments of the invention and the comparative examples and their properties and characteristics.

[0048] Table 1 lists properties and characteristics of compounds A to K (refrigeration oils) which are used by the embodiments of this invention and comparative examples. In the Table 1, PAO, POE, and PAG are respectively short for poly-α-olefin oil, hindered polyol ester oil (branched chain mixed fatty acid ester of pentaerythritol and di-pentaerythritol) and polyalkylene glycol oil (having dimethyl ether at both ends of polypropylene) in this order.

[0049] Table 2 is a list to show a test items for the heat-pump hot-water boiler which uses a refrigeration oil of the embodiment 1 of the invention and those for the heat-pump hot-water boiler which uses refrigeration oils of the comparative examples 1 to 3 for comparison. As shown in the Table 2, the refrigeration oil of the embodiment 1 is a mixture of 80 % by weight of compound A (PAO) and 20 % by weight of compound B (POE). The comparative example 1 uses compound A (PAO) which is one of the components of the refrigeration oil for the embodiment 1. The comparative example 2 uses compound B (POE) which is one of the components of the refrigeration oil for the embodiment 1. The comparative example 3 uses compound C (PAG) which is a main refrigeration oil for the carbon dioxide refrigerant. These refrigeration oils are respectively sealed in the boiler system and tested actually.

[0050] Here will be explained test items of the refrigeration oils in the actual service test. It is very important to suppress abrasion of the compressor for assurance of the compressor reliability. For this purpose, the inventors measured the increment of a clearance due to abrasion caused by test running between the bearing and the shaft, taking the worn-out status of the compressor into consideration. The size of the clearance between the bearing and the shaft is proportional to the quantity of abrasion. In general, as the clearance becomes greater, the shaft and the bearing generate more vibrations and noises. Further, the inventors checked the quantity of the refrigeration oil left in the compressor after testing and measured the total acid number of the refrigeration oil used for the test. In general, it is said that the quantity of the refrigeration oil returned to the compressor becomes less and causes deterioration of lubrication in the sliding section as the refrigeration oil is less compatible with the refrigerant.

[0051] For measurement of a leak current, the terminals of one filter circuit were respectively connected to the a.c. power supply and grounding, and the a.c. voltage between the terminals of the other filter circuit was measured. The leak current value is obtained by dividing the measured a.c. voltage by a resistance of 1 kΩ. As the leak current becomes greatest at the start-up of the boiler, the inventors measured the leak currents for 1 minute after the boiler started and selected peaks among the current leaks. Table 2 lists such current leak peaks. Further, the inventors measured the coefficient of performance (COP) of each boiler and listed the COP values relative to that of the comparative example 3 is 100 % standard).

[0052] The target of this test is to satisfy all of the following evaluation values:

Increment of clearance due to abrasion between the bearing and the shaft: 15 μm or less
Leak current: 1.0 mA or less
Quantity of the refrigeration oil in the compressor: no decrease after testing
COP: 100 % or more (relative to COP of the comparative example 3 (100 %)
Total acid value: 0.1 mg KOH/g or less

[0053] Table 2 shows the results of evaluations of the embodiment 1 and the comparative examples 1 to 3. In the Table 2, a value enclosed in parentheses indicates the content (% by weight) of a component in the oil mixture. Table 2 also lists up the dielectric constants and the viscosity indexes of the refrigeration oils used by the embodiments and the comparative examples. As seen in Table 2, the refrigeration oil of the embodiment 1 can suppress abrasion more than the refrigeration oils of the comparative examples 1 and 2. Therefore, the refrigeration oil of the embodiment 1 can assure high reliability of the boiler. As for leak currents, the boiler using the refrigeration oil of the embodiment 1 has a negligible current leak but the boiler using the refrigeration oil of the comparative example 3 has a great current leak which may cause electric shocks. As seen in Table 2, the dielectric constants are dependent upon the kinds of the refrigeration oils. Particularly, the polyalkylene glycol oil of the comparative example 3 is poor in electric characteristics. As for the quantity of refrigeration oil returned to the compressor, the boiler using the refrigeration oil of Embodiment 1 is almost the same as the boiler using the refrigeration oils of the comparative examples 2 and 3 which are compatible with carbon dioxide, assuring the refrigeration oil return to the compressor, sufficiently. The refrigeration oil of the comparative example 1 which was not compatible with the refrigerant was stagnating much in the cold area between the electric expansion valve 3 and the air heat exchanger 4 of the refrigeration cycle. This greatly reduced the quantity of the refrigeration oil in the compressor and caused abrasion in the compressor.

[0054] Since the carbon dioxide refrigerant is not soluble compound A in the oil mixture of the embodiment 1, the compression section of the compressor of the boiler using this refrigeration oil is satisfactorily sealed and as the result, the boiler has higher COP than the boiler using the refrigeration oil of the comparative example 3. Contrarily, since the carbon dioxide refrigerant is highly soluble to the refrigeration oil of the comparative example 2, a lot of the refrigeration oil moved from the compressor into the refrigeration cycle and as the result, the heat exchange efficiency of the boiler was reduced.

[0055] Naturally, the solution viscosity of the refrigeration oil became low, since the refrigerant is highly soluble to the refrigeration oil. This cannot assure the sealing of the compression section of the compressor and the resulting decrease of COP. As for the total acid numbers, the refrigeration oil of the embodiment 1 is low enough, but the polyol ester oil of the comparative example 2 is very high because of oil deterioration due to hydrolysis.

[0056] When only one kind of the refrigeration oil is used singly as seen in the comparative examples 1 to 3 in Table 2, all target evaluation items of the boiler cannot be satisfied. The same results as those of the embodiment 1 can be obtained by mineral oils instead of the poly-α-olefin oil although it is not shown in Table 2.

(Embodiment 2 to Embodiment 6)

[0057] Table 3 is lists to show a test items for the heat-pump hot-water boiler which uses refrigeration oils of the embodiments 2 to 6 of the invention and those for the heat-pump hot-water boiler which uses refrigeration oils of the comparative examples 4 to 6 for comparison. The test conditions of these embodiments are the same as those of the embodiment 1 except that the ambient temperature is 7 °C in the intermediate temperature condition, which is lower than the temperature of the embodiment 1. The test results are listed in Table 3. The test items of Table 3 are the same as those of Table 2.

[0058] The embodiment 2 to the embodiment 6 respectively use a mixture of the compounds A and the compounds B whose performances are already recognized by the embodiment 1 wherein the concentrations of the compounds A and the compounds B are changed. The comparative example 4 uses a refrigeration oil which contains less than 5 % by weight of the compound B in the mixture of the compounds A and the compounds B. The comparative example 5 uses a refrigeration oil which contains 70 % by weight or more of the compound B in the mixture of the compounds A and the compounds B. The comparative example 6 uses the compound C which is a main refrigeration oil for the carbon dioxide refrigerant. These refrigeration oils are respectively used in the boiler system and tested actually as same as the above.

[0059] The test results of the embodiments 2 to 6 and the comparative examples 4 to 6 are listed in Table 3. In Table 3, a value enclosed in parentheses indicates the content % by weight of a component in the oil mixture. Table 3 also lists up the dielectric constants and the viscosity indexes of the refrigeration oils used by the embodiments and the comparative examples. As seen in Table 3, the boilers using refrigeration oils of the embodiments 2 to 6 of the invention can reduce the increment of clearance due to abrasion between the bearing and the shaft and eliminate a current leak much more than the refrigeration oil of the comparative example 6 by making the content of the compound B (POE) 5 to 70 % by weight. The refrigeration oil can assure the quantity of the refrigeration oil return to the compressor sufficiently, and improve or retain the COP of the boiler relative to the COP of the comparative example 6. Further, the inventors recognized that the total acid numbers of the refrigeration oils of the embodiments 2 to 6 after tests were suppressed.

[0060] Contrarily, when the refrigeration oil of the comparative example 4 contains 3 % by weight of compound B (POE), the clearance between the bearing and the shaft becomes greater because the refrigerant oil is not compatible with carbon dioxide and the refrigeration oil returned to the compressor becomes less. Further, as shown in the comparative example 5, when the refrigeration oil of the comparative example 4 contains more than 70 % by weight of compound B (POE), the carbon dioxide refrigerant is greatly soluble in the refrigeration oil. This increases the quantity of the refrigeration oil transported from the compressor into the refrigeration cycle and reduces the heat exchange efficiency of the boiler. Further, the solution viscosity of the refrigeration oil became low, since the refrigerant is highly soluble to the refrigeration oil. This cannot assure the sealing of the compression section of the compressor. This reduces the COP and increases the total acid number of the refrigeration oil.

[0061] In this way, the boiler can satisfy all test items when using a refrigeration oil which contains 5 to 70 % by weight of the compound B (polyol ester oil) to the compound A (poly-α-olefin oil). Therefore, the ratio of the compound B to the compound A in the oil mixture should preferably be 10 to 30 % by weight considering the compatibility and the resistance to hydrolysis of the oil mixture.

(Embodiment 7 to Embodiment 9)

[0062] Table 4 is a list to show the test items for the heat-pump hot-water boiler which uses refrigeration oils of the embodiments 7 to 9 of the invention and those for the heat-pump hot-water boiler which uses refrigeration oils of the comparative examples 7 to 9 for comparison. The test conditions of these embodiments are the same as those of the embodiment 1 except that the ambient temperature is -5 °C in the winter temperature condition and lower than the temperature condition of the embodiments 2 to 6. The test results are listed in Table 4. The test items of Table 4 are the same as those of Table 2.

[0063] Each of the embodiments 7 to 9 was tested using the fixed ratio of 80 % by weight of the compound A (poly-α-olefin oil) and 20 % by weight of the compound B (polyol ester oil) whose performances were recognized by the embodiments 2 to 6 while the viscosity of the mixture was varied. The embodiment 7 used a refrigeration oil mixture of 80 % by weight of the compound D (PAO) and 20 % by weight of the compound E (see Table 1). The embodiment 8 as well as the embodiment 1 used a refrigeration oil mixture of 80 % by weight of the compound A and 20 % by weight of the compound B. The embodiment 9 used a refrigeration oil mixture of 80 % by weight of the compound F (PAO) and 20 % by weight of the compound G (POE). The viscosities of these refrigeration oil mixtures were 5 to 15 mm^2/s.

[0064] Meanwhile, the comparative example 7 used a refrigeration oil mixture of 80 % by weight of the compound H (PAO) and 20 % by weight of the compound I (POE). The comparative example 8 used a refrigeration oil mixture of 80 % by weight of the compound J (PAO) and 20 % by weight of the compound K (POE). The viscosities of these refrigeration oil mixtures were less than 5 mm^2/s and more than 15 mm^2/s. The comparative example 9 used a refrigeration oil which contains the compound C (PAG) only.

[0065] Table 4 shows the results of evaluations of the embodiments 7 to 9 and the comparative examples 7 to 9. A value enclosed in parentheses indicates the content % by weight of a component in the oil mixture. Table 4 also lists up the dielectric constants and the viscosity indexes of the refrigeration oils used by the embodiments and the comparative examples. As seen in Table 4, the boilers using refrigeration oils of the embodiments 2 and 6 can reduce the increment of clearance due to abrasion between the bearing and the shaft and eliminate a current leak much more than the refrigeration oil of the comparative example 9 by controlling the viscosity of the oil mixture which contains PAO (poly-α-olefin oil) and POE (polyol ester oil) in the range of 5 to 15 mm^2/s. The refrigeration oil can assure the quantity of the refrigeration oil return to the compressor sufficiently, and improve or retain the COP of the boiler relative to the COP of the comparative example 9. Further, the inventors recognized that the total acid numbers of the refrigeration oils after tests were suppressed.

[0066] Contrarily, when the boiler uses a refrigeration oil mixture whose viscosity is less than 5 mm^2/s in the comparative example 7, the clearance between the bearing and the shaft increases because of insufficient oil film formation. This cannot assure the sealing of the compression section of the compressor and the resulting decrease of COP. Oppositely, if the viscosity of the oil mixture is too high shown in the comparative example 8, the viscosity resistance and mechanical loss of the compressor increase and as the result, the COP goes down.

[0067] Judging from the test results of the embodiments 7 to 9, the boiler can satisfy all test items by controlling the viscosity of the refrigeration oil mixture which contains PAO (poly-α-olefin oil) and POE (polyol ester oil) in the range of 5 to 15 mm^2/s.

(Embodiment 10)

[0068] Table 5 is a list to show the test items for the heat-pump hot-water boiler which uses a refrigeration oil of the embodiment 10 of the invention and those for the heat-pump hot-water boiler which uses a refrigeration oil of the comparative example 10 for comparison. The test conditions of the embodiment 10 are the same as those of the embodiment 1 except that the ambient temperature is -15 °C in the severe winter temperature condition and lower than the temperature condition of the embodiments 7 to 9. The test results are listed in Table 5. The test items of Table 5 are the same as those of Table 2.

[0069] The embodiment 10 like the embodiment 8 uses a mixture of 80 % by weight of compound A (PAO) and 20 % by weight of compound B (POE). The comparative example 10 like the comparative example 9 uses compound C (PAG) which is a main refrigeration oil for the carbon dioxide refrigerant.

[0070] As seen in Table 5, the inventors found that the refrigeration oil mixture of the embodiment 10 was a little inferior in increment of the clearance between the bearing and the shaft, leak current, and total acid number to the embodiment 8, but satisfied the quantity of the refrigeration oil return to the compressor sufficiently, and excelled the COP of the boiler relative to the COP of the comparative example 10. Judging from this, it is found that the refrigeration oil of the embodiment 10 is available at very low temperature of -15 °C.

[0071] From the results of tests of boilers using the refrigeration oils of the embodiments 1 to 10, it is possible for the boilers to secure the quantity of the refrigeration oil return to the compressor sufficiently, suppress abrasion of the sliding parts of the compressor, reduce the dielectric constant of the refrigeration oil below 3.0, and suppress the leak current below a regulated permissible value. Further, since the quantity of the refrigeration oil returning to the compressor is assured sufficiently, the COP of the boiler can be improved.

[0072] Although the boiler of the embodiments uses a high-pressure chamber scroll type compressor as the enclosed motor-driven compressor, this invention is not limited to this. The same effect can be obtained by a 2-stage compression rotary compressor or a swing type compressor which contains rollers and vanes in a body.

Table 1

COMPOUND SYMBOL		A	B	C	D	E	F	G	H	I	J	K
COMPOUND NAME (ABBREVIATED)		PAO	POE	PAG	PAO	POE	PAO	POE	PAO	POE	PAO	POE
DENSITY (g/cm^3)	15°C	0.84	0.96	1.00	0.83	0.95	0.84	0.99	0.82	0.94	0.84	0.98
VISCOSITY (mm^2/s)	40°C	69	101	113	30	32	100	165	15	16	155	218
	100°C	10.4	10.7	21.5	5.8	5.2	13.8	16.3	3.7	3.3	19.1	21.1
DIELECTRIC CONSTANT		2.2	3.3	5.0	2.2	3.1	2.2	3.8	2.3	3.3	2.1	4.3
VISCOSITY INDEX		139	87	224	136	89	139	102	140	62	140	115

Table 2

		REFRIGERATION OIL		VISCOSITY OF OIL MIXTURE (mm2/s) 100°C	DIELECTRIC CONSTANT	VISCOSITY INDEX	BEARING CLEARANCE INCREMENT (μm)	LEAK CURRENT (mA)	RESIDUAL OIL	COP(%)	TOTAL ACID NUMBER (mgKOH/g)
		COMPONENT (1)	COMPONENT (2)								
EMBODIMENT	1	A(80)	B(20)	10.5	2.3	128	5	0.80	OK	102	0.02
COMPARATIVE EXAMPLE	1	A(100)	-	10.4	2.1	139	18	0.70	REDUCED	100	0.01
	2	B(100)	-	10.7	3.3	87	16	0.90	OK	98	0.12
	3	C(100)	-	21.5	5.0	219	7	1.30	OK	100 (REFERENCE)	0.01
( ): INDICATES THE CONTENT (% BY WEIGHT) OF A COMPONENT IN THE REFRIGERATION OIL MIXTURE.											

Table 3

		REFRIGERATION OIL		VISCOSITY OF OIL MIXTURE (mm2/s) 100°C	DIELECTRIC CONSTANT	VISCOSITY INDEX	LEAK CURRENT (mA)	BEARING CLEARANCE INCREMENT (μm)	RESIDUAL OIL	COP (%)	TOTAL ACID NUMBER (mgKOH/g)
		COMPONENT (1)	COMPONENT (2)								
EMBODIMENT	2	A(95)	B(5)	10.4	2.2	136	0.80	6	OK	100	0.02
	3	A(90)	B(10)	10.4	2.3	133	0.80	6	OK	101	0.02
	4	A(80)	B(20)	10.5	2.4	128	0.80	6	OK	102	0.02
	5	A(70)	B(30)	10.5	2.5	123	0.85	7	OK	102	0.03
	6	A(30)	B(70)	10.6	3.0	103	0.85	9	OK	101	0.06
COMPARATIVE EXAMPLE	4	A(97)	B(3)	10.4	2.1	137	0.75	18	REDUCED	99	0.01
	5	A(10)	B(90)	10.7	3.2	92	0.95	17	OK	98	0.13
	6	C(100)	-	21.5	5.0	219	1.35	8	OK	100 (REFERENCE)	0.01

( ): INDICATES THE CONTENT (% BY WEIGHT) OF A COMPONENT IN THE REFRIGERATION OIL MIXTURE.

Table 4

		REFRIGERATION OIL		VISCOSITY OF OIL MIXTURE (mm^2/s) 100°C	DIELECTRIC CONSTANT	VISCOSITY INDEX	BEARING CLEARANCE INCREMENT (μm)	LEAK (mA)	RESIDUAL OIL	COP (%)	TOTAL ACID NUMBER (mgKOH/g)
		COMPONENT (1)	COMPONENT (2)								
EMBODIMENT	7	D(80)	E(20)	5.7	2.4	127	10	0.85	OK	100	0.02
	8	A(80)	B(20)	10.4	2.3	128	8	0.85	OK	102	0.02
	9	F(80)	G(20)	14.2	2.5	132	5	0.90	OK	101	0.02
COMPARATIVE EXAMPLE	7	H(80)	I(20)	3.6	2.6	124	17	0.90	OK	98	0.01
	8	J(80)	K(20)	19.4	2.9	135	6	0.95	OK	98	0.05
	9	C(100)	-	21.5	5.0	219	13	1.45	A LITTLE REDUCED	100 (REFERENCE)	0.01

( ): INDICATES THE CONTENT (% BY WEIGHT) OF A COMPONENT IN THE REFRIGERATION OIL MIXTURE.

Table 5

		REFRIGERATION OIL		VISCOSITY OF OIL MIXTURE (mm2/s) 100°C	DIELECTRIC CONSTANT	VISCOSITY INDEX	BEARING CLEARANCE INCREMENT (μm)	LEAK CURRENT (mA)	RESIDUAL OIL	COP (%)	TOTAL ACID NUMBER (mgKOH/g)
		COMPONENT (1)	COMPONENT (2)								
EMBODIMENT	10	A(80)	B(20)	10.5	2.3	128	10	0.95	OK	103	0.03
COMPARATIVE EXAMPLE	10	C(100)	-	21.5	5.0	219	16	1.55	REDUCED	100 (REFERENCE)	0.02
(): INDICATES THE CONTENT (% BY WEIGHT) OF A COMPONENT IN THE REFRIGERATION OIL MIXTURE.											

Claims

1. Heat-pump hot-water boiler having a refrigeration cycle to circulate a carbon dioxide refrigerant, comprising:

   - an enclosed type motor driven compressor (1A, 1B) to take in and compress the refrigerant,
   - a first heat exchanger (2) to release heat of the refrigerant discharged from the compressor,
   - a decompressor (3A, 3B) to receive and decompress the refrigerant coming from the first heat exchanger (2),
   - a second heat exchanger (4A, 4B) to absorb heat of the refrigerant decompressed by the decompressor,
   - the first heat exchanger heating water up and supplying hot water therefrom, **characterized in that** the refrigeration oil for the enclosed type motor driven compressor (1A, 1 B) is a mixture of oils which are controlled to have a dielectric constant of up to 3.0.

2. Heat-pump hot-water boiler according to claim 1, **characterized in that** the refrigeration oil is a mixture of an oil being highly compatible with carbon dioxide and an oil being less compatible with carbon dioxide.

3. Heat-pump hot-water boiler according to claim 2, **characterized in that** the oil being highly compatible with carbon dioxide is a polyol ester oil, preferably a sterically hindered polyol ester oil, and the oil being less compatible with carbon dioxide is a poly-α-olefin oil and/or a mineral oil.

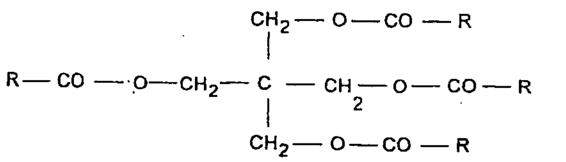
4. Heat-pump hot-water boiler according to claim 3, **characterized in that** the mineral oil is a naphthene-based mineral oil or a paraffin-based mineral oil or a mixture thereof.

5. Heat-pump hot-water boiler according to any of claims 1 to 4, **characterized in that** the refrigeration oil has a kinematic viscosity of 5 to 15 mm^2/s at 100 °C and a viscosity index of 100 or more.

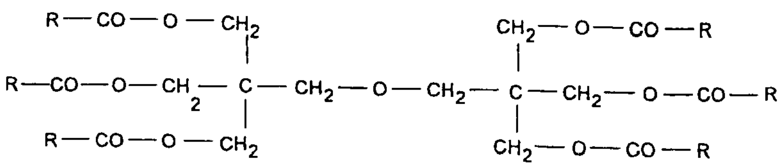
6. Heat-pump hot-water boiler according to any of claims 3 to 5, **characterized in that** the polyol ester oil is based on a polyhydric alcohol, preferably a sterically hindered polyhydric alcohol, and one or more monohydric fatty acids.

7. Heat-pump hot-water boiler according to any of claims 3 to 6, **characterized in that** the polyol ester oil is a branched-chain mixed fatty acid ester of pentaerythritol and/or dipentaerythritol.

8. Heat-pump hot-water boiler according to any of claims 3 to 7, **characterized in that** the polyol ester oil has the following formula (1) and/or (2),



(1),



(2),

   wherein R, which may be the same or different, is a linear or branched-chain alkyl group of 4 to 11 carbon atoms.

9. Heat-pump hot-water boiler according to any of claims 3 to 8, **characterized in that** the content of the polyol ester oil in the refrigeration oil is 5 to 70 % by weight.

10. Heat-pump hot-water boiler according to any of claims 3 to 9, **characterized in that** the content of the poly-α-olefin oil and/or the mineral oil in the refrigeration oil is 95 to 30 % by weight.

11. Heat-pump hot-water boiler according to any of claims 3 to 10, **characterized in that** the refrigeration oil consists of
95 to 30 % by weight of a poly-α-olefin and/or a mineral oil
and
5 to 70 % by weight of a polyol ester oil
and preferably consists of
90 to 70 % by weight of a poly-α-olefin and/or a mineral oil
and
10 to 30 % by weight of a polyol ester oil.

12. Heat-pump hot-water boiler according to any of claims 3 to 11, **characterized in that** the refrigeration oil consists of 80 % by weight of a poly-α-olefin oil and/or a mineral oil
and
20 % by weight of a polyol ester oil.

13. Refrigeration oil for compressors, particularly for refrigerators, air conditioning systems, heat-pumps and heat-pump heating systems such as heat-pump hot-water boilers, wherein carbon dioxide is used as refrigerant, **characterized in that** the refrigeration oil is a mixture of oils which is adjusted such that the dielectric constant thereof is up to 3.0.

14. Refrigeration oil according to claim 13, **characterized in that** it is a mixture of an oil being highly compatible with carbon dioxide and an oil being less compatible with carbon dioxide.

15. Refrigeration oil according to claim 13 or 14, **characterized in that**

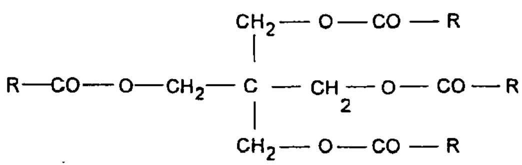
- the oil being less compatible with carbon dioxide is a poly-α-olefin and/or a mineral oil,
and
- the oil being highly compatible with carbon dioxide is a polyol ester oil, preferably a sterically hindered polyol ester oil.

16. Refrigeration oil according to any of claims 13 to 15, **characterized in that** it has a kinematic viscosity of 5 to 15 mm^2/s at 100 °C and a viscosity index of 100 or more.

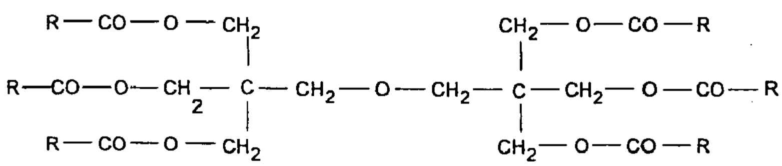
17. Refrigeration oil according to claim 15 or 16, **characterized in that** the polyol ester oil is based on a polyhydric alcohol, preferably a sterically hindered polyhydric alcohol, and one or more monohydric fatty acids.

18. Refrigeration oil according to any of claims 15 to 17, **characterized in that** the polyol ester oil is a branched-chain mixed fatty acid ester of pentaerythritol and/or dipentaerythritol.

19. Refrigeration oil according to any of claims 15 to 18, **characterized in that** the polyol ester oil has the following formula (1) and/or (2),



(1),



(2),

wherein R, which may be the same or different, is a linear or branched-chain alkyl group of 4 to 11 carbon atoms.

20. Refrigeration oil according to any of claims 15 to 19, **characterized by** one or more of the following features:

- The content of the polyol ester oil in the refrigeration oil is 5 to 70 % by weight;
- the content of the poly-α-olefin and/or the mineral oil in the refrigeration oil is 95 to 30 % by weight;
- the refrigeration oil consists of 95 to 30 % by weight of a poly-α-olefin and/or a mineral oil

and
5 to 70 % by weight of a polyol ester oil
and preferably consists of
90 to 70 % by weight of a poly-α-olefin and/or a mineral oil
and
10 to 30 % by weight of a polyol ester oil;
the refrigeration oil most preferably consists of
80 % by weight of a poly-α-olefin and/or a mineral oil
and
20 % by weight of a polyol ester oil.

FIG. 1

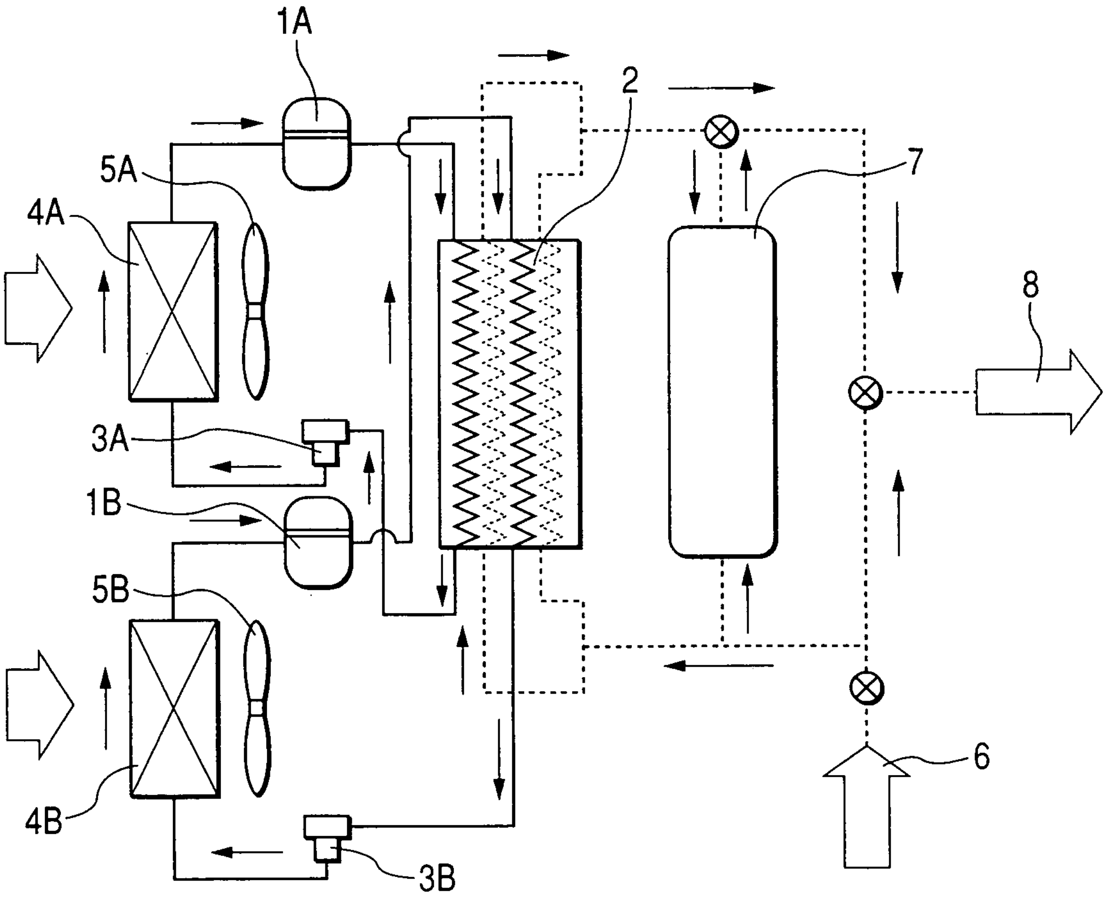


FIG. 2

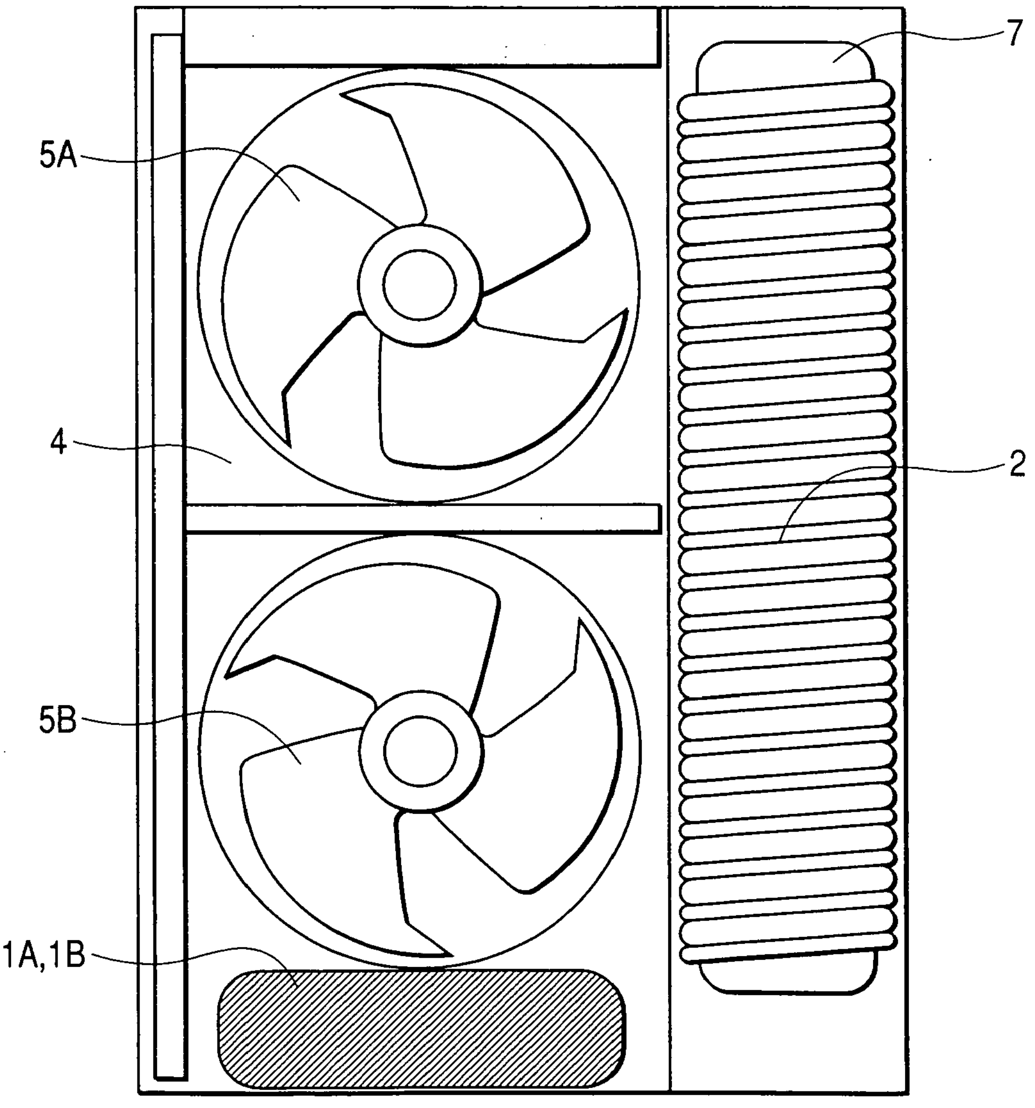
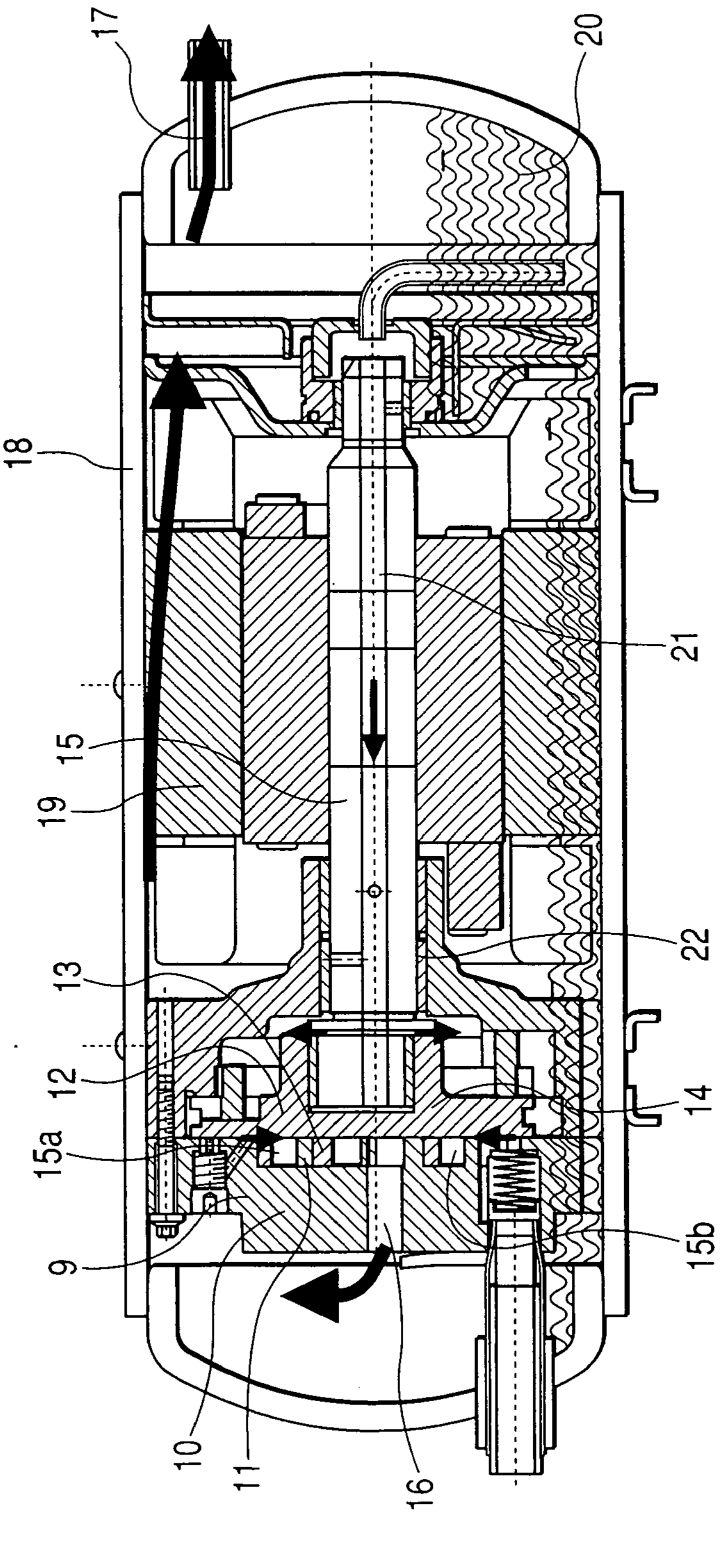


FIG. 3

1A,1B



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EUROPEAN SEARCH REPORT

Application Number
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The present search report has been drawn up for all claims

3

Place of search	Date of completion of the search	Examiner
Munich	5 September 2006	Kazemi, P

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