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71 Applicant: KABUSHIKI KAISHA TOSHIBA 72, Horikawa-Cho Salwai-ku Kawasaki-shi Kanagawa-ken (JP)

72 Inventor : Kitaichi, Shoichiro, c/o intellectual Property Div Kabushiki Kaisha Toshiba, 1-1, Shibaura

1-chome

Minato-ku, Tokyo (JP)

Inventor: Machida, Tadao, c/o Intellectual

**Property Division** 

Kabushiki Kaisha Toshiba, 1-1, Shibaura

1-chome

Minato-ku, Tokyo (JP)

Inventor: Sato, Shinobu, c/o Intellectual

**Property Division** 

Kabushiki Kaisha Toshiba, 1-1, Shibaura

1-chome

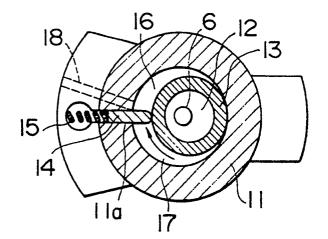
Minato-ku, Tokyo (JP)

(74) Representative: BATCHELLOR, KIRK & CO. 2 Pear Tree Court Farringdon Road London EC1R 0DS (GB)

(54) Refrigerant compressor for HFC 134a and components therefor.

A refrigerant compressor for using HFC 134a as a refrigerant and a refrigerator oil such as polyether type oil, polyester type oil, or similar type compatible therewith is disclosed. The refrigerant compressor includes a component of iron type substrate having a compound layer mainly made of iron sulphide on sliding portions such as sliding parts and the shaft in the compression mechanism. In a rotary type compressor, the sliding blade can have such a compound layer at its sliding surface. The hardness of the compound layer mainly made of iron sulphide can be considerable, substantially reducing metal contact and preventing adhesive abrasion; the primary cause of abrasion of sliding portions. Since such a compound layer essentially consisting of iron sulphide is stable under moist conditions, even if used in conjunction with polyether type oil, polyester type oil, or similar types of oil and HFC 134a, corrosion and abrasion through dissolution of the compound layer can also be largely prevented.

F I G. 2



### REFRIGERANT COMPRESSOR FOR HFC 134a AND COMPONENTS THEREFOR

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The present invention relates to a refrigerant compressor using HFC 134a as a refrigerant, and components therefor.

Generally, a room air conditioner, automobile air conditioner, refrigerator, and so forth use a refrigerant compressor for blowing cold air or hot air. As refrigerant compressors, hermetic type refrigerant compressor, automobile type semi-hermetic refrigerant compressor, and so forth are known.

For example, the hermetic, rotary type refrigerant compressor is provided with a motor mechanism and a compression mechanism which are disposed in an hermetic casing. The motor mechanism and the compression mechanism are connected by a shaft. The compression mechanism is driven by the motor mechanism through the shaft.

The compression mechanism is eccentrically fixed by both a cylinder or the like and the shaft. The compressor is provided with a roller rotatably disposed in the cylinder. In addition, a blade which pierces through the cylinder is provided. By the resilient force of a spring, one end of the blade is in contact with the outer periphery of the roller so as to divide the inside of cylinder into an inlet chamber and an outlet chamber. The roller is planetary moved by the rotation of the shaft. The planetary motion of the roller causes the refrigerant to be compressed. The compressed refrigerant is discharged into the casing and then supplied from an outlet pipe on the casing to the refrigerator. The sliding portion between the roller and the cylinder is lubricated with refrigerator oil filled in the casing to ensure smooth movement and operation. The shaft is similarly lubricated.

As refrigerants for the aforementioned refrigerant compressors, dichloro-difluoromethane (hereinafter named CFC 12) and chloro-difluoromethane have been mainly used. In addition, as refrigerator oils, naphthene type mineral oil and paraffin type mineral oil which are soluble in CFC 12 or chloro-difluoromethane have been used.

However, recently, it becomes clear that 'fluons' discharged from refrigerants can damage the ozone layer and thereby adversely affect the human body and biotic system. Thus, it is proposed to limit and eventually prohibit the use of CFC 12 and similar 'Fluons' which are severely damaging to the ozone layer.

Substitutes for CFC 12, namely 1, 1, 1, 2-tetrafluoroethane (hereinafter named HFC 134a) and 1, 1difluoroethane (hereinafter named HFC 152a) have been developed. Thus, compressors adapted for such refrigerants are strongly desired. For example, HFC 134a is almost insoluble in mineral oil which is a conventional refrigerator oil. Thus, as refrigerator oils, polyether type oil, polyester type oil, fluoride type oil, and so forth have been used.

However, when HFC 134a is used as a refrigerant and polyether type oil, polyester type oil, or the like which is soluble in HFC 134a is used as a refrigerator oil, the abrasion resisting property of sliding portions in the compression mechanism and so forth would be substantially degraded and thereby the refrigerant compressor could not be operated for a long and stable life. In other words, the conventional iron type materials (FC25, S-12C, S-15C, SWRCH10A, SWCH15A, SCM435H, and so forth), sintered alloy, stainless steel, and so forth would be excessively abraded.

The abrasion of the parts in the refrigerant compressor can be roughly categorized as shaft abrasion and blade abrasion in the compression mechanism. The blade is rubbed on the inner surface of the through hole in the cylinder by the pressure difference of the two chambers and thereby both the blade and the cylinder are abraded. In addition, since the end of the blade urged on to a roller by a spring, the outer periphery of the spring is also abraded. On the other hand, the shaft is exposed to the pressure of the spring and the cylinder and thereby it bears against the frame and bearing which support it.

Thus, since the shaft is rotated at a high speed while it is slightly bent, the outer surface of the shaft and the inner surfaces of the frame and the bearing are abraded likewise. When the sliding parts are abraded, the performance of the refrigerant compressor is degraded.

It is considered that the abrasion of the sliding ports takes place because the hygroscopic property of HFC 134a and the refrigerator oil which meets it is high. Conventionally, since a refrigerant and a refrigerator oil are directly circulated in the casing, when the amount of moisture therein increases, the sliding parts are increasingly abraded thereby disturbing normal operation of the refrigerant compressor.

As another factor for increasingly abrading the sliding parts, the following can be also considered. When CFC 12 is used as a refrigerant, Cl atoms in CFC 12 act on Fe atoms in metal substrate thereby forming an iron chloride film which has high abrasion resistance.

On the other hand, when HFC 134a is used, since CI atoms are not present, a lubricating film such as iron chloride film is not formed. Moreover, the iron chloride film can become dissolved in the presence of water and HCI may be produced. Since corrosion and abrasion of the substrate are increased, it is impossible to form an abrasion resisting film such as the iron chloride film in advance.

Consequently, refrigerant compressors using HFC 134a as a refrigerant and a refrigerator oil, which

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is soluble therein, such as polyether type oil or polyester, should have high abrasion resistance of the sliding parts and have high durability.

Thus, an object of the present invention is to provide a refrigerant compressor wherein the sliding portions thereof have high abrasion resisting property and high durability so as to be capable of using HFC 134a as the refrigerant.

To solve such problems, the refrigerant compressor according to the present invention uses HFC 134a as a refrigerant, the compressor having one or more components of an iron type substrate including a compound layer mainly made of iron sulphide on the sliding surface which acts as a sliding part.

The refrigerant compressor according to the present invention comprises a motor mechanism having a drive section, a compression mechanism having a cylinder and a moving member, the moving member being in contact with the cylinder and compressing the refrigerant, the compression mechanism being housed in an hermetic vessel cortaining refrigerator oil, a shaft connecting the drive section of said motor mechanism with the moving member of the compression mechanism, for transferring a drive force produced by the motor mechanism to the compression mechanism.

In such a refrigerant compressor, the sliding parts according to the present invention are used as parts of the shaft or the like. The sliding parts in the compression mechanism include the cylinder, rotor and piston (the rotor and piston being the moving parts). The sliding parts of the rotary type compressor include the blade and the rotary chamber. It is not always necessary to form a compound layer mainly made of iron sulphide on the entire surfaces of such sliding parts. It is possible to derive the benefits of the compound layer by employing it at a portion where a high load is applied in use.

The hardness of a chemical compound layer mainly made of iron sulphide is high. The compound can effectively prevent metals from contacting each other and can thereby prevent adhesion which is the major cause of abrasion. In addition, since the melting point is high (approx. 1000°C), the compound layer, which may be in the form of a thin film can be stable up to a very high temperature without breakage. In addition, since the compound mainly made of iron sulphide is stable in moist conditions, even if polyether type oil and HFC 134a, both of which can absorb water, are used, the film is not dissolved thereby preventing or minimizing corrosion and abrasion.

Thus, by using an iron type substrate having a compound layer mainly made of iron sulphide on the surface as compounds which are or which include sliding parts of refrigerant compressors which use HFC 134a as a refrigerant and polyether type oil or polyester type oil with compatibility therewith as a refrigerator oil, the abrasion resisting property of the slid-

ing portions can be maintained for a long time. Thus, it is possible to provide a refrigerant compressor which can operate for a long time, the refrigerant compressor using HFC 134a.

In order that the invention may be illustrated and readily carried into effect, several embodiments will now be described in detail by way of non-limiting examples only and wherein:

FIG. 1 is a vertical sectional view showing an enclosed rotary type refrigerant compressor,

FIG. 2 is a horizontal sectional view showing a compression mechanism of the refrigerant compressor shown in FIG. 1;

FIG. 3 is a sectional view showing the structure of a sliding part used in a refrigerant compressor; FIG. 4 is a table showing volume specific resistance of each lubricating oil;

FIG. 5 and FIG. 6 are a table and a graph showing hygroscopicity of lubricating oils and water solubility of 'fluons';

FIG. 7 is a graph plotting change of abrasion with increasing sulphur content in a refrigerator oil;

FIG. 8 is a diagram showing the result of X ray photo-electron spectroscopic analysis of the surface of a shaft according to an embodiment of the present invention;

FIG. 9 is a sectional view outlining the structure of an abrasion test machine used in testing embodiments of the present invention;

FIG. 10 and FIG. 11 are graphs showing the result of abrasion testing; and

FIG. 12 and FIG. 13 are charts showing the abrasion test result according to another embodiment of the present invention.

Referring to the accompanying drawings,

FIG. 1 is a vertical sectional view showing an enclosed rotary type refrigerant compressor according to an embodiment of the present invention.

In the figure, the reference numeral 1 is an enclosed casing. In the casing 1, a motor mechanism 4 is provided, the motor mechanism 4 comprising a stator 2 and a rotor 3, which is a drive section. At the lower section of the motor mechanism 4, a compression mechanism 5 is disposed. The motor mechanism 4 and the compression mechanism 5 are connected by a shaft 6. The drive force by the motor mechanism 4 is transferred through the shaft 6 so as to drive the compression mechanism 5.

When the compression mechanism 5 is driven, a refrigerant sent from a supply pipe 7 through an accumulator (not shown in the figure) is compressed. After the refrigerant is temporarily discharged to the casing 1, it is supplied to the refrigerator through an outlet pipe 8 disposed at the upper section of the casing 1. As the aforementioned refrigerant, HFC 134a (HFC 134a: 1, 1, 1, 2-tetrafluoroethane) is used.

Referring to FIG. 2 along with FIG. 1, the compression mechanism 5 is described

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The shaft 6 which is rotated by the motor mechanism 4 is supported by a bearing of the frame 9. The lower section of the shaft 6 is supported by a subbearing 10.

The shaft 6 is disposed so that it pierces through the cylinder 11 of the compression mechanism 5. At the shaft 6 in the cylinder 11, a crank section 12 (eccentric portion) is fixed. Between the crank section 12 and the cylinder 11, a roller 13 is engaged. The roller 13 is planetary-moved as the shaft 6 is rotated.

On the other hand, in the cylinder 11 a movable blade 14 is located. The blade 14 is disposed in a through hole 10a of the cylinder 11. The blade 14 is pressed by a spring 15. The blade 14 is reciprocally moved in accordance with the planetary motion of the roller 13. One end of the blade 14 contacts the outer periphery of the roller 13 by the resilient force of the spring 15 and thereby dividing the cylinder 11 into an inlet chamber 16 and an outlet chamber 17. The aforementioned refrigerant is sucked from an inlet port 18 and then compressed in accordance with the planetary motion of the roller 13 by the rotation of the shaft 6.

At the lower section of the casing 1, refrigerator oil 19 is contained. The refrigerator oil 19 is sucked by a pump (not shown in the figure) disposed at the lower end of the shaft 6 and thereby lubricating the sliding portion as the shaft 6 rotates.

The refrigerator oil 20 in the casing 1 should be compatible with HFC 134a used as the refrigerant to prevent the refrigerator oil from remaining in the refrigerating cycle and to securely restore the refrigerator oil to the compressor.

However, since HFC 134a has high polarity, it is not soluble at all in conventional mineral oils such as paraffin type oil, naphthene type oil, and alkylbenzene. Examples of refrigerator oils with compatibility with HFC 134a are polyether type compound, polyester type compound, fluorine type oil, and so forth. However, since fluorine type oil is expensive, it is not generally used in quantity.

On the other hand, although the compatibility of polyether type compound is not superior to that of high viscosity oil, polyalkylene glycolether type oil has high viscosity and high flow rate at low temperature. Thus, it is said that polyalkylene glycolether type oil is practically suitable for HFC 134a. In addition, it is possible to use a mixed oil of the aforementioned polyether type oil and naphthene type mineral oil, paraffin type mineral oil, alkylbenzene, or the like. Thus, the moisture absorption by polyether type oil can be prevented. In addition, to improve the hygroscopic property of oil and volume specific resistance, it is possible to use polyester type oil. In addition, it is possible to use a mixed oil of polyester type oil and naphthene type mineral oil, paraffin type mineral oil, alkylbenzene, or the like. FIG. 4 shows volume specific resistance of each lubricating oil.

The sliding portions in the refrigerant compressor according to the embodiment, in other words, the sliding portion lubricated with the aforementioned refrigerator oil are as follows.

The shaft 6 is exposed to the pressure of the spring 15 and the cylinder 11 through the roller 13 and thereby the shaft 6 is urged against the frame 9 and the sub-bearing 10. Thus, the shaft 6 is rotated in a slightly curved shape at a high speed. Consequently, the contacting portions between the outer surface of the shaft 6 and the frame 9 and between the shaft 6 and the inner surface of the sub-bearing 10 become sliding portions.

Since the blade 14 contacts the inner surface of the through hole 14a in the cylinder 11 by the pressure difference of the two chambers in the divided cylinder 11, the contacting portion between the blade 14 and the cylinder 11 becomes a sliding portion. In addition, since one end of the blade 14 is urged against the roller 13 by the spring 15, the contacting portion with the outer surface of the roller 13 becomes a sliding portion.

In the refrigerant compressor according to the present embodiment, for the aforementioned sliding portions, sliding parts where a compound layer 22 chiefly made of iron sulphide is formed on the respective component made of an Fe type metal substrate 21 are used.

The water solubility of HFC 134a is high. The hygroscopic property of refrigerator oils such as polyether type oil, polyester type oil, and the like is very high. FIGS. 5 and 6 are diagrams showing the hygroscopic property and the water solubility of each lubricating oil, respectively. In other words, the water solubility of the conventional CFC 12 is low. On the other hand, the hygroscopic property of the conventional mineral oil used along with CFC 12 is low. Thus, the iron chloride layer formed on the Fe metal substrate surface is so stable that it can prevent the Fe metal substrate from being abraded. However, in the system which uses HFC 134a and a refrigerator oil which is compatible therewith, since the hygroscopic property is very high, the iron chloride film becomes unstable and thereby it does not satisfactorily work as the abrasion resisting film.

To solve such a problem, in the present invention, a compound layer mainly made of iron sulphide is used as an abrasion resisting film. The compound film layer chiefly made of iron sulphide is so hard that it can satisfactorily prevent metals from being contacted. Thus, it is possible to prevent adhesion which is a major cause of metal abrasion. In addition, since the melting point of the compound is high (approx. 1000 °C), the film is stable up to a remarkably high temperature without breakage. In addition, since the compound layer mainly made of iron sulphide is stable in moist conditions, even if polyalkylene glycol type oil or polyether type oil and HFC 134a are used, the film is

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not dissolved so substantially minimizing or even preventing corrosion and abrasion. Thus the abrasion resisting property of the sliding portions in the aforementioned environment can be surprisingly improved and thereby the refrigerant compressor can be operated for a long and stable life.

The preferable thickness of the compound layer chiefly made of iron sulphide is approximately 0.001 um or more. A more preferable thickness of the compound layer is in the range approximately 0.1 µm to approximately 50 µm. When the thickness of the compound layer chiefly made of iron sulphide is less than  $0.001 \mu m$ , since it is too thin, the absorption resisting property cannot be satisfactorily obtained. On the other hand, when the thickness of the compound chiefly made of iron sulphide is more than 50 µm, since it is too thick, the accuracy of the dimensions of the refrigerant compressor may be decreased. Although the compound layer mainly made of iron sulphide may contain a small amount of a compound of phosphorus or other minor compound in the refrigerator oil as well as iron sulphide, such compound may not substantially alter the desirable properties of the compound layer mainly made of iron sulphide.

In addition, it is possible to provide an absorption layer, as a secondary layer, formed by a fatty acid such as stearic acid on the primary compound layer mainly made of the aforementioned iron sulphide. This secondary absorption layer may be obtained by reaction with a compound chiefly made of iron oxide or iron sulphide under aqueous conditions such as to form an iron soap. By the aggregation force which works between hydrocarbon chains, strength of the oil film can be improved. Since the shearing force of such secondary absorption film is small, the frictional coefficient thereof becomes low. Moreover, when the primary compound layer is a composed layermainly made of iron sulphide, since the absorption heat of stearic acid is high, the strength and the absorption resisting property of the oil film can be further improved.

The compound layer mainly made of iron sulphide can be practically formed on the following sliding surfaces of various components, e.g. the outer surface of the shaft 6, the inner surfaces of the frame 9 and the sub-bearing 10, the outer surface of the blade 14, the inner surfaces of the cylinder 11 and the through hole 14a thereon, the outer surface of the roller 13, and so forth. It is not always necessary to form the compound layer chiefly made of iron sulphide so that it covers the entire outer surfaces of the shaft 6 and the blade 14. When the compound layer is substantially formed at the sliding portions, the abrasion resisting property can be satisfactorily improved. For example, the sliding portion of the shaft 6 is the portion where it contacts the frame 9 and the sub-bearing 10. On the other hand, the sliding portion of the blade 14 is the portion where it contacts the through hole 14a provided in the cylinder 11 and the tip end of the blade 14 which contacts the roller 13.

The primary compound layer chiefly made of iron sulphide can be, for example, formed in the following manner

- (1) The component(s) having sliding part(s) are made of Fe type substrate. Sulphur is added to a refrigerator oil. While the refrigerant compressor is being operated, iron on the surface of the Fe type substrate which includes the sliding portion is chemically reacted with sulphur in the refrigerator oil. Thus, the compound layer mainly made of iron sulphide is formed.
- (2) By means of a sulphur penetration process or the like, the compound layer mainly made of iron sulphide is formed on the surface of the sliding part. Examples of sulphur penetration process, include a gaseous reaction method using a mixed gas comprising  $N_2S$  and  $NH_3$ ; liquid reaction method by adding sulphur or a suitable sulphur compound and by means of neutral or deductive salt bathing method; solid reaction method by heating sulphur in a solid agent such as FeS, graphite, or similar in a method corresponding to a solid cementation method; and electrolyte reaction method using an electrolytic solution containing a sulphide.

The compound layer mainly made of such iron sulphide can be formed on the entire surface of the sliding part or only partially formed thereon by using an appropriate masking method.

The sulphur in the refrigerator oil in the method (1) above may be derived from one of the following methods.

- (a) A refrigerator oil containing a sulphur component as an additive is used.
- (b) A sulphur component is added to the refrigerator oil

Examples of additives containing sulphur, include, for example, cetyl methyl sulphide, dicetyl sulphide, sulphide  $\beta$ ,  $\beta'$ - dichrole dicetyl, cetyl thiocyanate, and dialkyl zinc dithio phosphate. In addition, it is possible to add an additive containing a sulphur component to naphthene type mineral oil, paraffin type mineral oil, alkylbenzene type mineral oil, or to dissolve or disperse it in polyether type oil or the like as a refrigerator oil. In such a mixed oil, it is possible to add sulphur.

The preferable final content of sulphur in the refrigerator oil is 0.01 weight % to 5 weight %. As shown in FIG. 7, when the content of sulphur in the refrigerator oil exceeds 5 weight %, the abrasion resisting property is decreased. A more preferred sulphur content is 0.01 weight % to 2 weight %. In addition, in the aforementioned refrigerator oil, it is possible to add a solid lubricant such as molybdenum disulphide, graphite, sulphur type or halide type extreme pressure additive, or abrasion resisting property improving

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agent.

When the refrigerant compressor is operated by using the aforementioned refrigerator oil, as the shaft is rotated, the bearing or other component under a heavy local load becomes hot. The refrigerator oil circulated in the refrigerant compressor is thermally solvated or otherwise activated at the hot temperature portion. By the chemical reaction of the Fe type substrate and the sulphur component in the refrigerator oil, a compound layer mainly made of iron sulphide is formed on the surface of the shaft.

In the aforementioned embodiment, the enclosed rotary type refrigerant compressor was exemplified. However the present invention is clearly not limited thereto. Rather, the present invention can be applied to various types of refrigerant compressors such as a semi-hermetic type refrigerant compressor, reciprocating type refrigerant compressor and so forth.

An embodiment of a refrigerant compressor having a shaft with a compound layer mainly made of iron sulphide is described hereunder.

#### **Embodiment 1**

An embodiment for forming a compound layer mainly made of iron sulphide by means of the method (1) above.

First, the shaft 6 of SCM415 material (chromic molybdenum) which was cut in a particular shape was degreased with acetone. Thereafter, by using the shaft 6, a refrigerant compressor corresponding to FIG. 1 was assembled. A refrigerator oil comprising 0.1 weight % of SP type additive such as sulphur or phosphorus in polyalkylene glycolether type oil was filled in the casing 1. By using HFC 134a (1, 1, 1, 2-tetra fluoroethane) as a refrigerant, the refrigerant compressor was operated for 500 hours.

When the refrigerant compressor was operated, by the eccentric rotation of the shaft 6, a high load was applied to the upper and lower edges of each bearing which supports the shaft 6. When the shaft 6 was rotated, the sliding portion became hot. Thus, the refrigerator oil circulated in the refrigerant compressor was chemically reacted at the high temperature portion. By the effect of the additive, a compound mainly made of iron sulphide was produced. Thus, the compound layer mainly made of iron sulphide was formed on the surface of the shaft.

As counterparts of the present invention, like the aforementioned embodiment, two types of refrigerant compressors were operated for 500 hours, one of which was a refrigerant compressor where only polyalkylene glycol was supplied (hereinafter named comparison 1) and other of which was a refrigerant compressor where HFC 134a was used as a refrigerant and paraffin type refrigerator oil was supplied (comparison 2). The shafts used in the comparisons were same as that of the embodiment.

After the operation was completed, the compounds on the sliding portions of the three shafts of the embodiment and comparisons 1 and 2 were analyzed by means of X ray photoelectron spectroscopic analysis. FIG. 8 shows the results of the analyses. The solid line in the figure represents the result of analysis of the embodiment; the one-dot line in the figure represents that of the comparison 1; and the two-dot line of the figure represents that of the comparison 2.

From the results of the analyses, it is clear that on the surface of the shaft of the embodiment, a compound layer mainly made of iron sulphide is formed; on the shaft of the comparison 1, only a thin iron oxide film is formed; and on the shaft of the comparison 2, an iron chloride film is formed.

Moreover, the surface of each shaft was observed by using a scanning electron microscope (SEM) after the operation was completed. As the results of observations, on the shafts of the embodiment and the comparison 2, there were substantially no traces of abrasion. On the other hand, on the shaft of the comparison 1, traces of abrasion were clearly observed.

In addition, by using an abrasion test machine shown in FIG. 9, the abrasion resisting property of the shafts was evaluated. In this machine, a shaft 31 is nipped by a pair of V blocks 32. By setting the nipping load of the V blocks 32 to a particular value and rotating the shaft 31, the amount of abrasion was measured. In this evaluation, under the condition where the rotation of the shaft was set to 290 rpm and combinations of refrigerants and refrigerator oils were changed, the evaluation was conducted. FIG. 10 shows the results of the evaluation.

As shown in FIG. 10, when only polyalkylene glycol type oil was supplied while HFC 134a was used, the shaft was remarkably abraded. On the other hand, when the compound layer mainly made of iron sulphide was formed, the amount of abrasion was small. In other words, by using a refrigerator oil where 0.1 weight % of sulphur is added to polyalkylene glycol type oil, the compound layer mainly made of iron sulphide formed on the surface of the shaft and thereby the amount of abrasion is reduced.

From the above result, in the refrigerant compressor using HFC 134a as a refrigerant, the sliding part on which the compound layer mainly made of iron sulphide is formed is particularly effective for improving the abrasion resisting property and thereby the life of refrigerant compressor can be prolonged.

#### Embodiment 2

An embodiment where a compound layer mainly made of iron sulphide is formed by means of salt bathing method corresponding to the aforementioned method (2).

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A shaft of SCM415 material which was cut in a particular shape was degreased. Thereafter, the shaft was dipped in a neutral salt bath where the salt bathing composition was 25 % of KCN and 75 % of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (while a chloride such as NaCl, KCl, BaCl<sub>2</sub> or the like was mixed) under conditions where the process temperature was 180 °C to 200 °C and the process time was 10 minutes to 20 minutes. By anode-electrolyzing the shaft, a compound layer mainly made of iron sulphide of thickness from 5  $\mu m$  to 10  $\mu m$  was formed on the surface of the shaft.

As a counterpart of the embodiment, a shaft on which the compound layer mainly made of iron sulphide was not formed was produced.

Part of each shaft was cut. Thereafter, by conducting the X ray photoelectron spectroscopic analysis (XPS analysis) on the surface layer, it was observed that the compound layer mainly made of iron sulphide was formed on the surface of the shaft of the embodiment.

In addition, by conducting the abrasion test in the same manner as the embodiment 1, the abrasion resisting property of the shaft was evaluated.

In the result, like the embodiment 1, the amount of abrasion of the shaft of the embodiment 2 on which the compound layer mainly made of iron sulphide was formed was small and thereby the abrasion resisting property thereof was high. FIG. 11 shows the result of the abrasion test. As shown in the figure, although the shaft of the embodiment on which the compound layer mainly made of iron sulphide on the surface was formed was initially very slightly abraded, thereafter the amount of abrasion was not increased. Thus, it is clear that even if the shaft is used for a long time, the amount of abrasion is small.

In addition, by using the shaft of the embodiment, a refrigerant compressor shown in FIG. 1 was assembled. Thereafter, HFC 134a (1, 1, 1, 2 - tetra fluoroethane) and polyalkylene glycolether type oil were supplied as a refrigerant and a refrigerator oil, respectively, and then a real machine test was conducted. In the result, the compound layer mainly made of iron sulphide was neither cracked nor peeled off from the shaft. The shaft was smoothly rotated at 10000 rpm. After the test operation was completed, the surface of the shaft was observed by means of the scanning electron microscope (SEM). In the result, traces of abrasion were virtually absent on the shaft of the embodiment. On the other hand, traces of abrasion were clearly observed on the shaft of the comparison.

In the aforementioned embodiments, polyether type oil was used as the refrigerator oil. Now, embodiments where polyester type oil is used as a refrigerator oil will be described.

### Embodiment 3

An embodiment where the compound layer mainly made of iron sulphide is formed by means of the method (1) above.

After the shaft 6 of SCM415 material which was cut in a particular shape was degreased with acetone, by using the shaft, a refrigerant compressor corresponding to FIG. 1 was assembled. In addition, 0.1 weight % of a refrigerator oil where SP type additive such as sulphur or phosphorus or compound thereof was added to polyester type oil, which was then filled in the casing 1. Thereafter, by using HFC 134a (1,1, 1, 2 - tetra fluoroethane), the refrigerant compressor was operated for 500 hours.

When the refrigerant compressor was operated, by the eccentric rotation of the shaft 6, a high load was applied to the upper and lower edge portions of each bearing which supports the shaft 6. As the shaft was rotated, high temperature portions occurred locally. Thus, the refrigerator oil circulated in the refrigerant compressor was chemically reacted at the high temperature portions and thereby the additive caused the compound layer mainly made of iron sulphide to be produced. Thus, the compound film layer mainly made of iron sulphide was formed on the surface of the shaft.

On the other hand, as counterparts of the embodiment, the refrigerant compressor where only polyester type oil was supplied (herein after named comparison 3) and the refrigerant compressor where HFC 134a of refrigerant and paraffin type refrigerator oil were supplied (herein after named comparison 4) were operated for 500 hours. The shafts used in the comparisons were the same as that of the embodiment.

After the operation was completed, compounds which were produced at the sliding portions on the shafts of the embodiment 3 and the comparisons 3 and 4 were evaluated by means of the X ray photoelectron spectroscopic analyzing method. The analyzed results were the same as those of the embodiment 1. On the surface of the shaft of the embodiment 3, the compound layer mainly made of iron sulphide was formed; on the shaft of the comparison 3, only a thin iron oxide film was formed; and on the shaft of the comparison 4, an iron chloride layer was formed.

After the operation was completed, the surfaces of the shafts were observed by means of the scanning electron microscope (SEM). In the result, on the shafts of the embodiment 3 and the comparison 4, traces of abrasion were virtually absent. On the other hand, on the shaft of the comparison 3, traces of abrasion were clearly observed.

Moreover, by using the abrasion test machine shown in FIG. 9, the abrasion resisting properties of the shafts were evaluated. The test was conducted by

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changing combinations of refrigerants and refrigerator oils in the condition where the rotation of each shaft was 290 rpm. FIG. 12 shows the result of the test

As shown in FIG. 12, when only polyester type oil was supplied while HFC 134a was used, the shaft became quite abraded. On the other hand, when the compound layer mainly made of iron sulphide was formed, the amount of abrasion was small. In other words, by using a refrigerator oil where polyester type oil containing 0.1 weight % of sulfur, a compound layer mainly made of iron sulphide is formed on the surface of the shaft and thereby the amount of abrasion is reduced.

Thus, it is clear that in the refrigerant compressor using HFC 134a as a refrigerant, sliding parts on which the compound layer mainly made of iron sulfide is effective for improving the abrasion resisting property and the life of the refrigerant compressor is prolonged.

#### **Embodiment 4**

An embodiment where polyester type oil is used as a refrigerator oil and the compound layer mainly made of iron sulphide obtained by means of a salt bathing method as in method (2) above.

Like the embodiment 2, a shaft of SCM415 material which was cut in a particular shape was degreased with acetone. Thereafter, the shaft was dipped in a neutral salt bath where the salt bathing composition was 25 % of KCN and 75 % of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (while a chloride such as NaCl, KCl, BaCl<sub>2</sub>, or the like was mixed) under conditions where the process temperature was 180 °C to 200 °C and the process time was 10 minutes to 20 minutes. By anode-electrolyzing the shaft, a layer mainly made of iron sulphide whose thickness was 5 $\mu$ m to 10 $\mu$ m was formed on the surface of the shaft.

As a counterpart of the embodiment, a shaft on which the compound layer mainly made of iron sulphide is absent, was produced.

Part of each shaft was cut. Thereafter, by conducting X ray photoelectron spectroscopic analysis (XPS analysis) on the surface layer, it was observed that the compound layer mainly made of iron sulphide was formed on the surface of the shaft of the embodiment.

In addition, by conducting the abrasion test in the same manner as the embodiment 1, the abrasion resisting property of the shaft was evaluated.

In the result, like the embodiment 1, the amount of abrasion of the shaft of the embodiment 2 on which the compound layer mainly made of iron sulphide was formed was small and thereby the abrasion resisting property thereof was high. FIG. 13 shows the result of the abrasion test. As shown in the figure, although the shaft of the embodiment on which the compound layer

mainly made of iron sulphide on the surface was formed was initially slightly abraded thereafter the amount of abrasion was not increased. Thus, it is clear that even if the shaft is used for a long time, the amount of abrasion is small.

In addition, by using the shaft of the embodiment, a refrigerant compressor shown in FIG. 1 was assembled. Thereafter, HFC 134a (1, 1, 1, 2 - tetra fluoroethane) and polyalkylene glycolether type oil were supplied as a refrigerant and a refrigerator oil, respectively, and then a real machine test was conducted. In the result, the compound layer mainly made of iron sulphide was neither cracked nor peeled off from the shaft. The shaft was smoothly rotated at 10000 rpm. After the test operation was completed, the surface of the shaft was observed by means of the scanning electron microscope (SEM). In the result, traces of abrasion were virtually absent on the shaft of the embodiment. On the other hand, traces of abrasion were clearly observed on the shaft of the comparison.

Claims

- A refrigerant compressor using HFC 134a as a refrigerant, including a sliding member of an iron type substrate which has a compound layer on a sliding surface as a sliding part, said layer mainly made of iron sulphide.
- 2. A refrigerant compressor using HFC 134a as a refrigerant, comprising:
  - a motor mechanism having a drive section:
  - a compression mechanism having a cylinder and a moving member, said moving member being in contact with said cylinder and compressing said refrigerant, said compression mechanism housed in an hermetic vessel containing refrigerator oil; and
  - a shaft for connecting the drive section of said motor mechanism and the moving member of said compression mechanism and for transferring a drive force produced by said motor mechanism to said compression mechanism, said shaft being of an iron type substrate which has a compound layer mainly made of iron sulphide at a part of the surface thereof.
- 3. A refrigerant compressor using HFC 134a as a refrigerant, comprising:
  - a motor mechanism having a drive section;
  - a compression mechanism having a cylinder and a moving member, said moving member being in contact with said cylinder and compressing said refrigerant, said compression member

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being housed in an hermetic vessel containing refrigerator oil, said compression mechanism being of an iron type substrate which has a compound layer mainly made of iron sulphide at a part of the surface thereof as a sliding member; and

a shaft for connecting the drive section of said motor mechanism and the moving member of said compression mechanism and for transferring a drive force produced by said motor mechanism to said compression mechanism.

- 4. A refrigerant compressor as claimed in any preceding claim, wherein the thickness of said compound layer is in the range from 0.001 μm to 50 μm.
- 5. A refrigerant compressor as claimed in any preceding claim, wherein said compound layer has been formed by chemically reacting sulphur contained in refrigerator oil within said refrigerant compressor with iron on the sliding surface of said iron type substrate when said refrigerant compressor has been operated.
- 6. A refrigerant compressor as claimed in claim 5, wherein said sulphur is contained in said refrigerator oil as an additive.
- A refrigerant compressor as claimed in claim 5 or
   wherein said refrigerator oil comprises polyether type oil and/or polyester type oil.
- 8. A refrigerant compressor as claimed in any one of claims 2 to 7, wherein said compression mechanism has a sliding portion and an iron type substrate with a compound layer mainly made of iron sulphide for use as a sliding part thereof.
- 9. A refrigerant compressor as claimed in any one of claims 3 to 8, wherein said compression mechanism has a blade for dividing said cylinder into an inlet chamber and an outlet chamber and a rotor for rotating said cylinder being divided by said blade, said compound layer being provided at least at a part of the inner surface of said cylinder, the outer surface of said blade, and the outer surface of said rotor.
- 10. A refrigerant compressor as claimed in any one of claims 3 to 9, wherein said shaft is of iron type substrate having a compound layer mainly made of iron sulphide.
- 11. A sliding part useful in a refrigerant compressor incorporating HFC 134a as a refrigerant, wherein said sliding part is of an iron type substrate having a compound layer mainly made of iron sulphide on its sliding surface.

12. A sliding part as claimed in claim 11, wherein the thickness of said compound layer is 0.001  $\mu m$  to 50  $\mu m$ .

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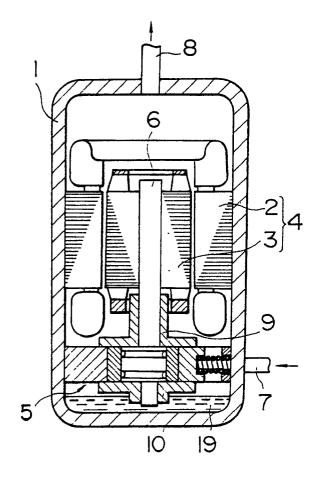
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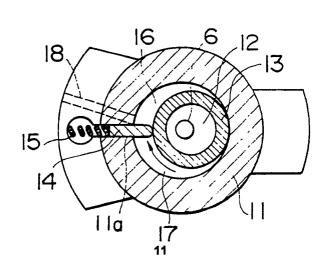
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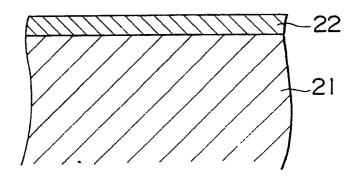
FIG.I



F I G. 2



F I G. 3



F | G. 5

### HYGROSCOPIC PROPERTY OF EACH LUBRICATING OIL (UNIT: ppm)

OIL	ESTER	POLY- ALKYLENE GLYCOL 1	POLY- ALKYLENE GLYCOL 2	POLY- ALKYLENE GLYCOL 2 - MINERAL OIL	CONVEN- TIONAL MINERAL OIL
0	109	335	352	211	29
24	1130	2763	4496	656	40
48	1380	4039	7031	1021	44
72	1433	4393	7771	1107	46
96	1502	4802	8233	1383	46

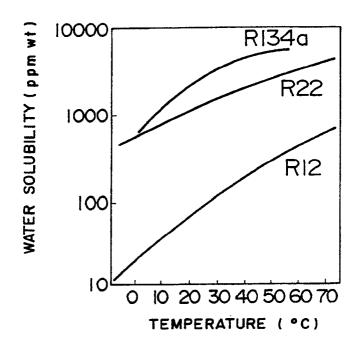
NOTE: TEMPERATURE : 25°C HUMIDITY: 70 %

# F I G. 4

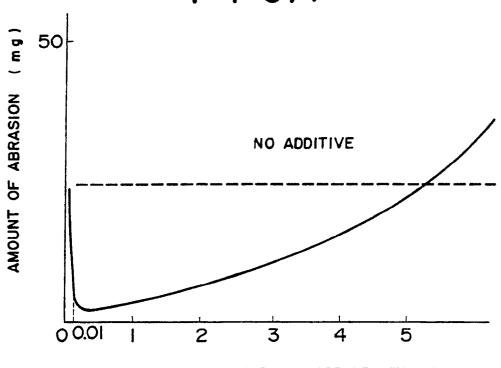
## VOLUME SPECIFIC RESISTANCE OF EACH LUBRICATING OIL

ESTER	POLYALKYLENE GLYCOL	MINERAL OIL	
1013	1010	10 <sup>14</sup>	

F I G.6

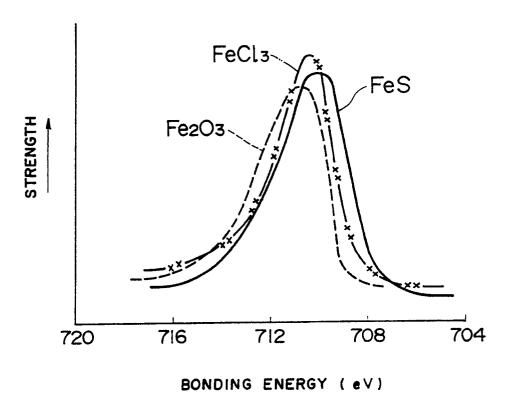


F I G.7

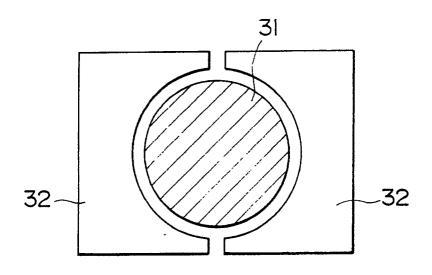


CONTENT OF SULFUR IN REFRIGERATOR OIL ( wt %)

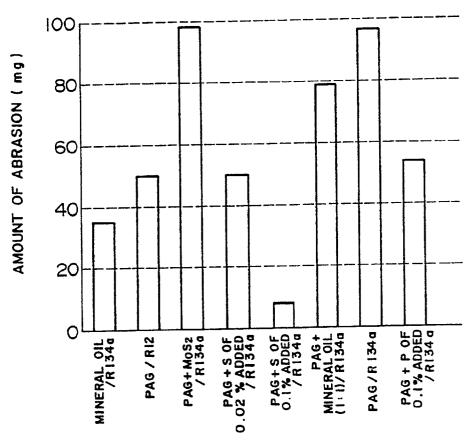
F I G.8



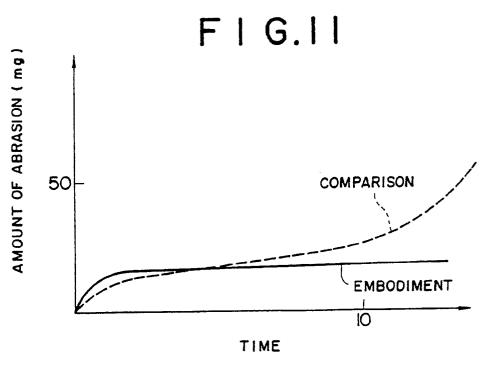
F1G.9



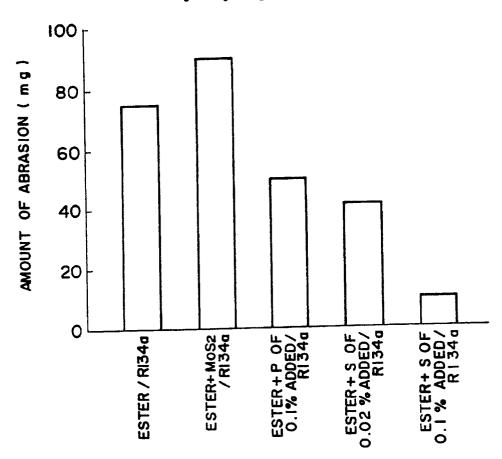
### F I G.10



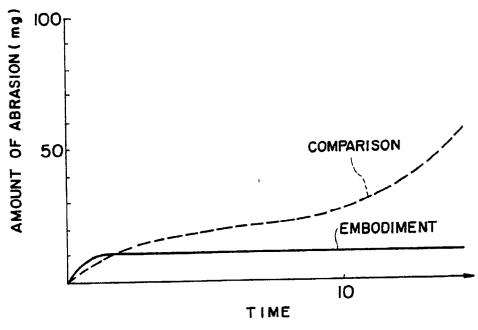
PAG = POLYALKYLENE GLYCOL ETHER



F I G. 12



F I G. 13





### **EUROPEAN SEARCH REPORT**

Application Number

EP 90 31 4364

ategory	Citation of document with in of relevant pas		Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
	FROID.  vol. 42, no. 654, 15 De pages 39 - 43; MARIOTON  "PREVENIR PLUT^OT QUE G  * the whole document *	cember 87, PARIS FR	1	F25B31/00 F04B39/02
.	GB-A-2074247 (WINKLER)  * the whole document *		1	
	GB-A-13266/1913 (KOVEN)	<b></b>		
	· <u></u> .			
				TECHNICAL FIELDS SEARCHED (Int. Cl.5 )
				F25B F04B F04C
	The present search report has b	een drawn up for all claims		
	Place of search	Date of completion of the search		Examiner
	THE HAGUE	05 APRIL 1991	VON	ARX H.P.
X : par Y : par doc	CATEGORY OF CITED DOCUMES ticularly relevant if taken alone ticularly relevant if combined with and ument of the same category anological background	E: earlier patent doc after the filing da other D: document cited in L: document cited fo	ument, but pub te the application r other reasons	lished on, or