(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 1 505 175 A1

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 158(3) EPC

(43) Date of publication:
09.02.2005 Bulletin 2005/06

(21) Application number: **02807291.6**

(22) Date of filing: **04.11.2002**

(51) Int Cl.[7]: **C23C 22/02**, F02F 3/00, F16J 1/00

(86) International application number:
PCT/CN2002/000784

(87) International publication number:
WO 2003/091478 (06.11.2003 Gazette 2003/45)

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR IE IT LI LU MC NL PT SE SK TR
Designated Extension States:
AL LT LV MK RO SI

(30) Priority: **26.04.2002 CN 02118621**

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(54) CHEMICAL SURFACE TREATMENT METHOD OF PISTON

(57) A chemical process for treating surface of a piston to reduce its surface friction includes immersing piston in machine oil, heating to 220-250°C, adding alkali-metal carbonate, alkali-metal nitrite, alkali-metal chloride, and Ce-containing rare-earth metal powder, maintaining said temperature for 10-24 hours, cooling to below 50°C and taking out the piston. The invention can be used to improve the pistons and the cylinders for various engines and air compressors. It can obviously improve the work efficiency of the piston and the cylinder and prolong the operational life of the whole cylinder. It can not only save fuel but also reduce exhaust pollution from vehicles and air compressors, which results in good prospect in industry.

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Description

TECHNICAL FIELD

[0001] This invention is related to a chemical process for treating surface of a piston. The treated piston can evidently reduce the friction between a piston ring groove and a piston ring and reduce the friction between a piston (especially piston skirt) and a cylinder wall. It will improve evidently the tightness of the cylinder and prolongs the operational life of the cylinder liner, the piston and the piston ring.

BACKGROUND ART

[0002] One of the main structures of an internal-combustion engine is a piston-connecting rod mechanism. The high-temperature and high-pressure gas generated by combustion of a fuel in the cylinder drives the piston to move downwards. Then the piston transfers the power to a crankshaft by a connecting rod to make the crankshaft rotate to apply work.

[0003] 3-4 piston ring grooves are formed on the piston in order to prevent gas leakage. There are piston rings in a piston ring groove. The piston ring is a circular alloy cast-iron ring. When the piston implements reciprocating motion, the piston ring clings to the cylinder all along so as to prevent the high-temperature and high-pressure gas get across between the piston ring and the cylinder wall, which has a sealing action.

[0004] The disadvantages of the piston design in prior art are as follows:

[0005] In order to lighten the weight of parts for reciprocating motion, the piston is generally manufactured by using aluminum alloy. But the expansion coefficient of aluminum alloy is larger than that of alloy cast-iron (the material of cylinder). In order to prevent the abrasion when the piston is heated and the piston clings to the cylinder excessively, the outer diameter of the piston skirt is sometimes designed to a form at which the lower diameter is larger than the upper diameter. It is like irregular taper with oval cross-section. The largest size of the piston skirt is smaller than the diameter of the cylinder. The clearance between the piston and the cylinder is about 0.02-0.08 % of the diameter of the cylinder in a gasoline engine and about 0.01-0.18 % of the diameter of the cylinder in a diesel engine. The effects of this clearance are as follows: 1. When the piston proceeds reciprocating motion it will swing causing the skirt and top of the piston strike the cylinder so as to increase the running noise of an internal-combustion engine; 2. The swing of the pistons will increase move of the piston ring in the piston ring groove so as to increase the abrasion of the piston ring groove and the piston ring and shorten the operational life; 3. The piston ring will move up and down in the ring groove if the piston ring groove is abraded. Then it will bring a pump-absorb effect on the lubricant resulting in the flow of lubricant to the top of the cylinder and the lubricant will take part in the combustion reaction, all of which make exhaust pollution and high consumption of the lubricant.

[0006] In order to improve the wear resistance and the mesh resistance of the piston and the piston ring, the piston and piston ring are commonly treated as follows: phosphatizing or nitriding the surface on the piston ring; porous chrome-plating or spraying of molybdenum on the parts clinging to the cylinder; tin-plating or spraying of graphite on the piston skirt and so on.

[0007] All of above treatments can not change the attrition essential caused by the half-dry slide of the piston. The piston ring and the cylinder at relatively high speed can not make the piston and the piston ring move in cylinder with non-slot or microgap. Thus the prior art treatments can't overcome radically the above shortcomings all along.

CONTENTS OF THE INVENTION

[0008] Accordingly, the objective of the present invention is to provide a chemical process for treating the surface of the piston that can overcome radically the above said disadvantages. Said process can evidently reduce the friction between the piston and cylinder wall and reduce the friction between the piston ring groove and the piston ring. It will leads to the movement of the piston in the cylinder with non-slot or microgap and the movement of the piston ring in the piston ring groove with microgap. Thus said process can obviously not only increase working efficiency of the cylinder but also prolong the operational life of the cylinder.

The present inventors have considered that the main reason why the movement of the piston and the piston ring in cylinder can not be non-slot or microgap is that the conventional surface treatment techniques can not evidently reduce the friction among the piston, the piston ring and the cylinder wall. According to lubrication theory, the lubrication mechanism of a lubricant is that it will form a layer of an oil-film on the surface of two parts against each other. It will leads to the change of the friction between the two parts from direct friction to sliding friction with the two layers of oil films. Lubricant, especially sold in the market as commodity at present, contains various additives. The additive having the function of lubrication is a kind of chain hydrocarbon with a polar group on one chain end. This polar group can adsorb on the surface of metals and make another end having non-polar group erect upwards. Thus a thicker layer of oil film can be formed to ensure the function of lubrication on the surface of the metal parts. Whereas, the adsorption of the polar group on a smooth surface of metals isn't quite firm even though the lubricant component has the polar group. The adsorption between the metal surface and lubricant component will be broken when two metal parts rub each other. In order to overcome the shortcoming, some reticular pattern for storing oil is honed on the cylinder wall to supply continuously the lubricant to the cylinder wall at prior art. But if the reticular pattern is too large and dense, the surface may be concavo-convex. thus the most of surfaces of cylinder wall and all surfaces of the piston should appear to be smooth, which can not keep the integrated oil-films in a cylinder strokes .

[0009] The present inventors think that if homogeneously distributed many invisible micro cavities are formed on at least one surfaces of the two mutual-friction metallic parts, not only can the micro cavities reserve lubricant, but also they can allow polar groups on the end of lubricant additive molecules to get into them and adsorb those molecules firmly. Thus integrated oil-films are kept in all of the cylinder strokes. Furthermore, the micro cavities will not affect smoothness of the metal surfaces and thus will not affect the free slip of the metal parts. The homogeneously distributed micro cavities can be formed on the surface of alloy aluminum as long as a micro-inhomogeneous weaker corrosive is found. Moreover, the present inventors think if some small rigid oil-absorbing particles exist in the cavities, they can roll freely in the cavities and produce roll-friction function because a layer of lubricant is absorbed surround the particles, which can further reduce the friction between the two metal parts. All of above were not reported at prior art. The present inventors have found the micro-inhomogeneous weaker corrosive suitable for chemical micro etching of surface on the alloy aluminum of the piston after plentiful tests. The present inventors have also found that Ce-containing rare-earth oxide powders (Cerium existing in general mixed rare-earth compound and the content of Cerium being up to 50%), especially the oxide particles made from Ce-containing metal powder through explosive oxidation reaction, have a rigid and porous structure. The powders can not only adsorb plentiful oil but also be not cracked during the rolling process, which have a function of freely rolling friction. So the friction between the metal parts is substantially decreased.

[0010] To achieve above said object, there is a chemical process for treating the surface of the piston to reduce its surface friction. The process includes immersing the piston in machine oil, heating the machine oil gradually to 220-250°C (preferably, 230-240°C) under the condition that the oil is not spilt, and adding the following to form a mixture:

alkali-metal carbonate(preferably, sodium carbonate)	0.3-1.0wt%
alkali-metal nitrite(preferably, sodium nitrite)	0.3-1.0wt%
alkali-metal chloride(preferably, sodium chloride)	0.20-0.60wt%
Ce-containing rare-earth metal powder (preferably, Ce metal powder) 1.0-1.6wt%	
Machine oil	rest;

then maintaining said temperature for 10-24 hours(preferably, 13-16 hours), cooling naturally to below 50°C and taking out the piston.

[0011] The % contents of the above said components are based on the total weight of all solid additives and machine oil.

[0012] The present invention will now be described in detail as follows:

[0013] The kinds of machine oil in said process are not especially limited as long as it is not obviously volatilizing under the temperature between 220°C and 250°C. And the heat-up rate is not also especially limited as long as it isn't too rapid and can avoid the oil spilt owing to the volatilization of water or impurity in machine oil. The quantity of machine oil should be supplied to the original level to ensure that the machine oil can immerse all parts when the oil is decreased and maintain the above said ratio of machine oil to each other component. Thus it can be seen that the heat-up time is prolonged along with the increase of quantity of machine oil, which is the reason why the heat-up time. is not limited.

alkali-metal carbonate (eg. sodium carbonate) and alkali-metal nitrite (eg. sodium nitrite and potassium nitrite) and alkali-metal chloride(eg. sodium chloride and potassium chloride) are all weaker corrosive materials. Their molecules are strong polar and yet the molecules of machine oil are non-polar so that the above said weaker corrosive materials can not dissolve in machine oil. But they can suspend in machine oil homogeneously in a finely divided state and thereby a micro inhomogeneous weak corrosive is formed, which is the reason why the present inventors select machine oil rather than water medium as carrier medium of micro etching. Owing to the synergistic effect of these corrosives, many homogeneously distributed micro cavities are formed on the surface of aluminum alloy in the piston. If the ratio of these corrosives to machine oil is too low in the mixture, the minimal requirements of the micro etching can not be met. But if the ratio of the corrosive to machine oil is too high, the micro cavities will be too large so as to affect the smoothness of the surface of aluminum alloy.

[0014] Moreover, rare-earth metals are active metals. They react easily with oxygen in air and then change to rare-earth oxide. Cerium dioxide is a kind of rigid particle so that it can be used as polishing compound. Cerium dioxide powder made by Cerium metal powder through explosive oxidation reaction has a porous and rigid structure. Due to this structure, this powder can adsorb plentiful lubricants and fall to the micro cavities on the surface of aluminum alloy and then roll freely. But Cerium dioxide powder made from Cerium metal powder through precipitation in water has not above said porous structure, which is main reason why the present inventors select Ce-containing rare-earth metal powder (preferably, Ce metal powder) rather than Cerium dioxide as reaction additive. The present inventors prepared a section of the piston surface-treated as described in this invention and observed the section by magnifying it 500 times under a microscope. It was seen. that there is an about 0.01mm thick layer of adhesion material on the surface of the piston. And it was observed by magnifying the section 2000 times under an electronic microscope that the adhesion material in a spherical state was rolling. It can be decided that the rolling particles in a spherical state are Ce-containing rare-earth oxide (especially, Cerium dioxide) according to chemical component and chemical reactive property of above said additives. The freely rolling of Ce-containing rare-earth oxide particles in the micro cavities on the surface makes the friction essential change from the conventional sliding-friction model to rolling-friction model as described in the present invention when the piston moves reciprocally in cylinder. Thus the friction between the metal surfaces is largely decreased. As described in above reasons, the friction between the piston ring and the piston ring groove is decreased in the same measure.

[0015] Of course, if similar etch for forming the micro cavity is used in the piston ring, the friction between the piston ring and the cylinder wall can be decreased and the friction between the piston ring and the piston ring groove can be further decreased. The material of piston ring is alloy cast-iron rather than alloy aluminum so that etch for forming the micro cavity on the piston ring is different from that on the piston according to the present invention. The technique for treating the piston ring is beyond the limits of this invention. Thus the present inventors will apply for another application.

[0016] If the operating temperature is less than 220°C, the rate of the etch for forming the micro cavity will be too low, it is disadvantageous for productivity. But if the operating temperature is more than 250°C, the rate will be too high, which will make the micro cavity too large and even affect the smooth property of the metallic surface on the whole. And the operating temperature that is more than 250 °C will lead to partial carbon deposit of machine oil so as to affect the uniformity of the etch for forming the micro cavity. Thus the operating temperature is limited to 220-250°C, preferably 230-240°C.

[0017] What's more, if the maintaining time at said operating temperature is less than 10 hours, the micro cavity can not be formed adequately. But if the maintaining time at said operating temperature is more than 24 hours, the micro cavity can be overly formed. Thus the maintaining time at said operating temperature is limited to 10-24 hours, preferably 13-16 hours.

[0018] Compared with the conventional surface treatment techniques, the present invention has the following advantageous effects:

I . The effect of present invention used in the overall design of the cylinder

1. The clearance between the piston and the cylinder wall is eliminated or reduced evidently. The clearance in a gasoline engine may be non-slot and that in a diesel engine may be microgap which is about 0.05-0.07 % of the diameter of cylinder that is a half of the conventional design;
2. The cost of the cylinder will reduce by using the cylinder without reticular pattern or the cylinder with shallower reticular pattern;

II . The advantageous effect of present invention used in the internal-combustion engine

1. The compressive force of the cylinder is increased, the ignition lag of the diesel is decreased and the power and economical performance is improved;
2. The consumption of lubricant and the exhaust of the diesel are reduced;
3. The operational life of the cylinder is prolonged by 1-2 times;
4. The cold-start ability is improved;
5. The idle speed stability enhanced;
6. The running noise is decreased;
7. There is not breakage of the oil-film on the surface of the cylinder and the cylinder scratch is decreased evidently;
8. The aging of the lubricant is delayed and the oil drain period is prolonged by one times;

III. The advantageous effect present invention used in the piston of an air compressor

1. The suction vacuum degree and the suction flow are increased and the seal performance of cylinder is improved;
2. The oil content in the compressed gas is decreased;
3. The operational life of the cylinder and the piston is prolonged by 1-2 times;

MODE OF CARRYING OUT THE INVENTION

[0019] This present invention is more specifically explained with reference to following embodiments and working examples. However, these examples are not to be construed to limit the scope of the present invention.

[0020] EXAMPLE 1: A piston of a gasoline engine was put in a metal container, said piston was immersed with 2330g 32# machine oil and electric-heated gradually to 235°C under the condition that the oil is not spilt. The following components were added to form a mixture by using a scoop within several times for about 15 minutes:

sodium carbonate	0.63wt% (15g)
sodium nitrite	0.63wt% (15g)
sodium chloride	0.42wt%(10g)
Ce metal powder	1.3wt% (30g)
and machine oil	97wt%(2330g)

[0021] The temperature was maintained at about 235°C for 14 hours, then was naturally cooled to 40°C and the piston was taken out.

[0022] The % contents of above components are based on the total weight of the whole solid additives and machine oil.

[0023] EXAMPIE 2: Conditions for the process are similar to the Example 1, except that the Ce metal powder was replaced by the Ce-containing rare-earth metal powder, in which the content of Ce is about 50 wt%.

[0024] EXAMPIE 3: Conditions for the process are similar to the Example 1, except that the piston of gasoline engine was replaced by a piston of diesel engine.

[0025] EXAMPIE 4: Conditions for the process are similar to the Example 1, except that the piston of gasoline engine was replaced by the piston of air compressor.

[0026] EXAMPIE 5: Conditions for the process are similar to the Example 2, except that the piston of gasoline engine was replaced by the piston of diesel engine.

[0027] EXAMPIE 6: Conditions for the process are similar to the Example 2, except that the piston of gasoline engine was replaced by the piston of air compressor.

WORKING EXAMPLE 1: The effect of the piston of a gasoline engine treated alone according to present invention

[0028] A piston of gasoline engine surface-treated as described above in Example 1 was used to improve the gasoline engine in a transit bus that belongs to CA6102 gasoline engine made from CHANGCHUN FIRST AUTOMOBILE ENGINE FACTORY of China. The original design of said engine is as follows:

$$\text{Diameter of cylinder} \times \text{stroke} = 101.6\text{mm} \times 114.3\text{mm}.$$

The design of the clearance space of the piston ring is as follows: the first air ring is between 0.5mm and 0.7mm; the second air ring is between 0.4mm and 0.6mm; the third air ring is between 0.4mm and 0.6mm and the fourth oil ring is between 0.3mm and 0.5mm. And the clearance between the piston and the cylinder is between 0.02mm and 0.06mm. The improved engine has the following design: the clearance space of the first air ring is 0.13mm and that of the second and the third air rings are 0.10mm and that of the fourth ring is 0.07mm. The cylinder liner is embedded to the original cylinder and then honed, which makes the clearance is between -0.02mm(that is, the size of piston skirt is larger than the inner diameter of cylinder) and 0(non-slot). The tests show that the suction vacuum degree is obviously increased and the dynamic and economic performances are obviously improved.

WORKING EXAMPLE 2: The effect of the piston of a diesel engine treated alone according to present invention

[0029] A piston of diesel engine surface-treated as described above in Example 3 was used to improve the diesel engine in a transit bus that belongs to D6114 diesel engine made from Shanghai Diesel Engine Factory of China. The original design of said engine is as follows:

$$\text{Diameter of cylinder} \times \text{stroke} = 114\text{mm} \times 135\text{mm}.$$

[0030] The design of the clearance space of the piston ring is as follows: the first air ring is between 0.4mm and

0.6mm; the second air ring is between 0.4mm and 0.6mm; the third oil ring is between 0.3mm and 0.5mm and the clearance is between 0.17mm and 0.23mm. The improved engine has the following design: the clearance space of the first air ring is 0.15mm and that of the second ring is 0.20mm and that of the third rings is 0.07mm. The clearance between the piston and the cylinder can be decreased to 0.09mm if the shallower reticular pattern cylinder liner having small diameter is used. The transit bus maintains excellent dynamic performance after driving for 25 thousand kilometer. The consumption of fuel is decreased by 8.0% when compared with untreated engine. And the consumption of the lubricant is obviously decreased. The oil drain period is prolonged one times. The free acceleration smoke is less than 2 and that is 5 according to national standard. The compressive force of the cylinder is increased by 20%. Inspect result after opening the engine is excellent. The cylinder liner has almost no wear. The wear quantity of the piston ring is very small and can be used again.

WORKING EXAMPLE 3: The effect of both piston and piston ring of gasoline engine treated synchronously

[0031] Both piston of gasoline engine surface-treated as described above in Example 1 and piston ring treated by similar etch for forming the micro cavity were used to improve the gasoline engine in a transit bus that belongs to CA6102 gasoline engine made from CHANGCHUN FIRST AUTOMOBILE ENGINE FACTORY of China. The result is better than the result of working example 1. For example, The improved engine has the following design: the clearance space of the first ring is decreased to 0.10mm and that of the fourth ring is decreased to 0.05mm. Thus it can be seen that the two clearance spaces (corresponding to 10-20 % of that before improving) are smaller than untreated those and smaller obviously than the least clearance between the piston in the present invention and conventional piston ring. The result of the driving tests on the transit bus is better than that of working example 1.

WORKING EXAMPLE 4: The effect of both piston and piston ring of diesel engine treated synchronously

[0032] Both piston of diesel engine surface-treated as described above in Example 3 and piston ring treated by similar etch for forming the micro cavity were used to improve the diesel engine in a transit bus that belongs to D6114 diesel engine made from Shanghai Diesel Engine Factory of China. The result is better than the result of working example 2. For example, The improved engine has the following design: the clearance space of the second ring is decreased to 0.18mm and the clearance between the piston and the cylinder is decreased to 0.07mm if the shallower reticular pattern cylinder liner having small diameter is used. Thus it can be seen that the two clearance spaces are smaller than untreated those and smaller obviously than the least clearance between the piston in the present invention and conventional piston ring. The result of the driving tests on the transit bus is better than that of working example 2.

INDUSTRIAL APPLICATION

[0033] The above examples show that the invention can be used to improve the pistons and cylinders for various engines (such as the gasoline engine and the diesel engine) and air compressors. It can obviously improve the work efficiency of the piston and the cylinder and prolong the operational life of the whole cylinder. It can not only save fuel but also reduce exhaust pollution from vehicles and air compressors, which results in good prospect in industry.

Claims

1. A chemical process for treating the surface of a piston to reduce its surface friction, which comprises the following sequential steps:

immersing the piston in machine oil, heating gradually to 220-250°C under the condition that the oil is not spilt, adding the following components to form a mixture:

alkali-metal carbonate	0.3-1.0wt%
alkali-metal nitrite	0.3-1.0wt%
alkali-metal chloride	0.20-0.60wt%
Ce-containing rare-earth metal powder	1.0-1.6wt%
machine oil	rest,

then maintaining said temperature for 10-24 hours, cooling naturally to below 50°C and taking out the piston, the % contents of above components basing on the total weight of the whole solid additives and machine oil.

2. The process according to claim 1, wherein said Ce-containing rare-earth metal powder is Ce metal powder.

3. The process according to claim 1, wherein said alkali-metal carbonate is sodium carbonate.

4. The process according to claim 1, wherein said alkali-metal nitrite is sodium nitrite.

5. The process according to claim 1, wherein said alkali-metal chloride is sodium chloride.

6. The process according to claim 1, wherein said operating temperature is between 230°C and 240°C.

7. The process according to claim 1, wherein the hold time of said operating temperature is between 13 hours and 16 hours.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN02/00784

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C23C22/02 F02F3/00 F16J1/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C23C22 F02F F16J1

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CN 1081742 A (LI JIFU), 9 February 1994 (9.2.1994) Abstract	1-7
A	CN 1096565 A (YIN XIANQUAN), 21 December 1994 (21.12.1994) the whole document	1-7
A	JP 8027580 A (TOYOTA JIDOSHA KK), 30 January 1996 (30.1.1996) Abstract	1-7
A	JP 7246365 A (TOYOTA JIDOSHA KK), 26 September 1995 (26.9.1995) Abstract	1-7

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
30.January 2003 (30.01.03)	13 FEB 2003 (13.02.03)

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Form PCT/ISA /210 (second sheet) (July 1998)

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN02/00784

Patent document Cited in search report	Publication date	Patent family members	Publication date
CN 1081742 A	9-2-1994	NONE	
CN 1096565 A	21-12-1994	CN 1033661 B	25-12-1996
JP 8027580 A	30-1-1996	NONE	
JP 7246365 A	26-9-1995	JP 3168810 B2	21-5-2001

Form PCT/ISA /210 (patent family annex) (July 1998)