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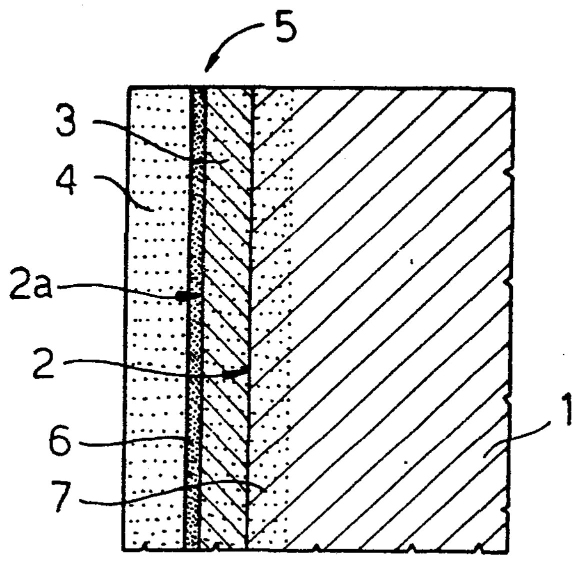
(54) **Mechanical element for the combustion chamber of a diesel engine of the type comprising sliding surfaces having wear protective layers for the running-in phase, and method for obtaining these layers.**

(57) A mechanical component (1), in particular for the combustion chamber of a diesel engine, having at least one sliding surface (2, 2a) coated with a wear-protective layer (4) which can be worn away during a running-in period and constituted by a nitride based heat diffusion layer nitrides with a percentage content by weight of nitrogen lying between about 4% and about 12%, which layer is obtained by a gaseous nitriding with ammonia or ionised nitrogen at temperatures less than or equal to about 600 °C.



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"MECHANICAL ELEMENT FOR THE COMBUSTION CHAMBER OF A DIESEL ENGINE OF THE TYPE COMPRISING SLIDING SURFACES HAVING WEAR PROTECTIVE LAYERS FOR THE RUNNING-IN PHASE, AND METHOD FOR OBTAINING THESE LAYERS"

The present invention relates to a mechanical element, in particular to a component for a combustion chamber of a high speed diesel engine, of the type having sliding surfaces provided with wear-protection layers which are used up during the running-in period, and to a process for obtaining such layers.

It is known that for the purpose of extending the life of diesel engines and the maintenance intervals thereof it is sought to encourage a correct running-in by means of the application of wear-protection layers on the sliding surfaces of the mechanical elements forming components of the engine, and in particular those forming the combustion chamber, such as the piston rings, cylinder sleeve, valve stems, valve seats, hollow pistons (in spheroidal or laminate cast iron, or steel), gudgeon pins, injectors and injection pumps. The protective layers currently used are constituted by electrolytically deposited layers of copper and/or tin, layers of phosphates and iron oxides produced by chemical reaction, or by organic or inorganic anti-friction layers (for example cresol resin with graphite).

The known wear-protection layers described above have the disadvantage of becoming rapidly destroyed so that they facilitate running-in only during the first hours of operation, whilst the running-in period necessary for engines can be up to even about 2000 hours.

The object of the present invention is to provide mechanical elements having sliding surfaces coated with wear-protection layers of high thermal stability, of high resistance to oxidation and corrosion, even in the presence of gas containing sulphur, and having low friction and long life.

The said object is achieved by the present invention in that it relates to a mechanical element forming a component of a combustion chamber of a diesel engine in particular, of the type comprising at least one sliding surface coated with a wear-protection layer which can be worn away during a running-in period, characterised by the fact that the said wear layer is constituted by a nitride based heat diffusion layer containing a percentage by weight of nitrogen lying between about 4% and 12%.

The present invention further relates to a process for forming a wear-protection layer over a sliding surface of an element forming a component of a combustion chamber of a diesel engine, which can be worn away during the running-in period of the said engine, characterised by the fact that it comprises a phase of gaseous nitriding of the said surface performed with ammonia or nitrogen ionised at a temperature less than or equal to 600^{o}C in conditions such as to obtain on the said surface the formation of a layer of nitrides substantially of ε - type.

For a better understanding of the present invention a non limitative description of an embodiment thereof will now be given with reference to the attached drawings, in which:

Figure 1 schematically illustrates a portion of a mechanical element provided with a sliding surface coated with a protective layer formed according to the principles of the present invention; and

Figures 2 and 3 are qualititive wear diagrams illustrating the wear of an element protected with the layer of Figure 1 and the same element protected with a conventional wear-protection layer respectively.

With reference to Figure 1 there is indicated a mechanical element 1 of any type having at least one sliding surface 2 cooperating frictionally with a similar sliding surface of another element; the element 1 can be constituted by any member forming a component of an engine and in particular by a member forming a component of or involved in the combustion chamber of a diesel engine, such as a piston ring, cylinder sleeve, valve stem or valve seat, a hollow piston for housing the piston rings (both pistons made of spheroidal or laminar cast iron, and those of steel), a gudgeon pin or an element of an injector or an injection pump.

The present invention can find application, equally, in one or all of the mechanical members listed above, and in particular to the piston rings which are among the mechanical elements most subjected to wear in an engine, and which have, as is known, three sliding surfaces 2 particularly subjected to wear, and constituted by the outer lateral surfaces thereof intended to cooperate by sliding against the wall of the cylinder sleeve to exercise a sealing action against the combustion gases on one side and the lubricating oil on the other, and by the upper and lower surfaces intended to engage against the walls of the hollow piston in which the piston ring is housed.

The said lateral surface 2 of the piston ring is preferably coated, as is illustrated in Figure 1, by a plasma sprayed layer 3 of a metal alloy and/or metal/ceramic (for example based on Cr-carbide or Mo-carbide, Cr and Nicr) of great hardness substantially greater than that of the material constituting the element 1; in this case the surface 2 does not work directly but serves solely as a support for the layer 3 an outer surface 2a of which constitutes the actual sliding surface of the element 1.

In either case, according to the invention, the sliding surface 2 or 2a is coated with a wear-protection layer 4 which can be worn away during a running-in period of the element 1, in such a way as to expose the surface 2 (or 2a) of great hardness at the end of the running in period. The layer 4 must have low friction and be relatively soft, of hardness substantially equal to or only slightly greater than that of the material from which the element 1 is made, and must at the same time have a hardness and a resistance to wear such as to allow it to last for a period at least equal to the running-in period of the element 1, which in the case of piston rings or other elements forming components of an engine, is of the order of 1000 hours of operation. Such characteristics are obtained, according to the invention, with wear layers 4 constituted by nitride based heat diffusion layers containing a percentage by weight of nitrogen lying between about 4% and about 12%, preferably being iron, chrome and molibdenum elements which give, with the nitrogen, nitrides having a quite satisfactory degree of heat stability, and with the element 1 being made of an alloy containing such elements (steel or cast iron), the layer 4 is based on nitrides of iron (and/or chrome or molibdenum) of the chemical formula Fe_xN where x is a number, even a decimal, the value of which must lie between two and four, and in particular, must be greater than or equal to two and less than four. Such chemical compounds are well known in the art under the name "white sheet" by which are meant solid ε and ξ type solutions of nitrogen in iron having compact hexagonal and rhombic structures respectively, and with nitrogen contents lying between 4% and 12%. At the maximum degree of nitriding the ε phase corresponds with a good approximation to the formula Fe_2N and, at a lower egree of nitriding, to the formula Fe_3N.

As is known, ε nitrides or "white sheet" are obtained as unwanted by-products of both liquid and gaseous conventional hard nitriding of mechanical elements, the object of which is to harden the surface thereof by the formation of an intermetallic γ' compound of the formula Fe_4N.

The principal known utilisation of ε nitrides has until now consisted in the preparation of layers of such nitrides by means of nitriding operations conducted at high temperatures (close to about 700°C)against the 590°C or a normal nitriding) on surfaces of elements subjected to corrosion by moisture, for the purpose of forming protective ε nitride layers which protect the elements against corrosion; in fact it was discovered that ε nitrides in saline solutions had cathodic potentials (about +0.10v NHE) which made them substantially impervious to attack by corrosive agents (protective nitriding).

Now, after numerous experimental tests, the applicant has surprisingly found that ε nitrides or "white sheet" particularly those of iron, have low coefficients of friction, high resistance to oxidation and high thermal stability, and an excellent resistance to wear in the particular chemical and physical conditions present in the combustion chamber of a heat engine, in particular both high speed and slow diesel engines, even in the presence of low quality fuels which generate sulphurous combustion gases rich in fuel ash. Comparative wear tests performed on piston rings provided with conventional electro-deposited wear layers of copper and tin and on piston rings provided with wear layers constituted by ε nitrides of iron have provided results set out in the semi-logarithmic diagrams of Figures 2 and 3; in particular in Figure 2 there is illustrated a qualititive diagram which plots the variation of wear (W) of a piston ring according to the invention with respect to a reference parameter β (preferably time in hours of operation, or else distance in Km travelled), whilst in Figure 3 there is illustrated a similar diagram which plots the variation of wear (W) of a conventional piston ring provided with an electro-deposited wear layer, with respect to the same reference parameter β . As can be seen from Figures 2 and 3 the said diagrams are each sub-divided into three sections, respectively a,b and c, relating, in order, to the running in period, to the main lifetime period of operation of the element, and to the end period in which collapse by wear takes place; the values of β are plotted on a logarithmic scale. With reference to Figure 2, for the whole of the section a of the associated diagram a substantially parabolic variation of W can be seen, which is free from discontinuities; at the end of the section a (about 1000 hours of operation) the variation of W is such as to join without discontinuity with the rectilinear section b. This corresponds to a lifetime of the layer 4 substantially equal to the running-in period of the element 1. On the other hand, in Figure 3 the section a has a discontinuity and is composed of a first curved section with strong inclination, corresponding to a period β of several tens of hours, and by a rectilinear section which constitutes an extension of the section b; this corresponds to a duration of the electro-deposited protection layer of several tens of hours only, compared with the running-in period of a thousand hours which involves, as can be seen by comparison of the two diagrams, a shorter overall lifetime of the element (the reduction of the lifetime is equal to the quantity α), and a greater wear in the running-in period. The same comparative tests have moreover permitted a significant reduction to be detected in the value of the coefficient of friction of the wear-protective layer according to the invention with respect to that of conventional electro-deposited layers.

The layer 4 of ε nitrides is obtained, according to the invention, by means of a particular gaseous nitriding treatment at low temperature (less than or equal to 500°C) performed in nitriding ovens in the form of autoclaves, in which the nitriding is performed by means of a gaseous fluid of ammonia (NH_3) or ammonia mixed with methane (CH_4) at an aboslute pressure lying between one and ten Torr (one Torr is approximately equal to 1 mm of mercury $\simeq$ 0.0013 atmospheres). In such ovens, in a known method, but applied to different technical fields, the elements to be nitrided are maintained at cathodic potential, whilst the metal walls of the oven are maintained at an anodic potential; between the walls and the elements there is then applied a potential difference sufficient to ionise the gaseous atmosphere between the anode and cathode. According to the invention the potential difference for performing the nitriding at the temperature indicated (less than or equal to 500°C) must be equal to or greater than 350v. With temperatures lying between about 350°C and 500°C pressures of one to ten Torr, potential differences of 380v or more and nitriding times lying between two and thirty hours, diffusion layers 5 of nitrogen are produced in the surface 2 of about 0.1 to 0.5 mm in thickness (Figure 1). The layer 5 comprises three successive layers, increasingly rich in nitrogen the further they are from the surface 2 (towards the outside) and in fact comprises the outermost layer 4 constituted by ε nitrides, followed by an immediately underlying layer 6 of monophasic γ' nitride having a formula Fe_4N, followed in turn by a diffusion layer 7 having a low nitrogen content (nitrogen-ferrite and nitrogen-austenite) similar to that which can be found on mechanical pieces subjected to the known TENIFER liquid nitriding process.

The layers 6 and 7 are obtained as an involuntary and inevitable consequence of producing the layer 4 and also involve the possible coating layer 3; it has been found that such supplementary layers 6 and 7 underlying the wear layer 4 and covering the surface 2, further improve both the mechanical characteristics and the resistance to wear of the element 1; in fact the layer 7 increases the resilience and the resistance to fatigue of the element 1 with an action similar to that of the diffusion layers which can be obtained with the TENIFER process, whilst the layer of γ' nitrides of thickness lying between two and fifteen micron and of much greater hardness than that of the base material of the element 1, protects the surface 2 from fretting corrosion after the wear layer 4 has been used up at the end of the running-in period, allowing possible coating layers of electrodeposited chrome to be dispensed with. In the case of a plasma coated layer 3 being present (based on chrome-molibdenum alloys of great hardness) this is also produced by introducing a percentage of iron into its composition in such a way that it can also form iron nitrides within it, whereby to obtain, simultaneously with the the formation of the layer 4, an increase in the hardness and mechanical, chemical and physical characteristics of the coating layer 3 and consequently of the sliding surface 2a.

Finally, thanks to the particular nitriding process used, it is possible to work at a temperature not greater than 500°C, thereby avoiding possible deformations of the element 1; this is particularly important for the piston rings which are easily subject to thermal deformations, for which a hard nitriding treatment, or worse, a "protective nitriding" of conventional type would be entirely unsuitable because of the high temperatures at which such treatments are performed.

(Dr. Ing. PRATO Roberto)

CLAIMS

1. A mechanical element (1) forming part of a combustion chamber of a diesel engine, of a type comprising at least one sliding surface (2,2a) coated with a wear-protection layer (4) which can be worn away during a running-in period, characterised by the fact that the said wear layer (4) is constituted by a nitride based heat diffusion layer containing a percentage by weight of nitrogen lying between about 4% and 12%.

2. An element (1) according to Claim 1, characterised by the fact that the said heat diffusion layer is based on iron nitrides of chemical formula Fe_xN where x is a number greater than or equal to two and less than four.

3. An element (1) according to Claim 1 or Claim 2, characterised by the fact that immediately beneath the said wear-protection layer (4) the said surface (2,2a) is coated with an anti-wear layer (6) of single phase nitride of thickness lying between two and fifteen microns, and a hardness greater than that of the material with which the said element is made.

4. An element (1) according to Claim 3, characterised by the fact that the said anti-wear layer (6) is constituted predominantly by iron nitride of formula Fe_4N.

5. An element (1) according to any preceding Claim, characterised by the fact that the said wear-protection layer (4) has a hardness substantially equal to or greater than that of the material of which the

said element (1) is made.

6. An element (1) according to any preceding Claim, characterised by the fact that beneath the said wear-protection layer (4) the said surface (2) is coated with a plasma sprayed layer (3) of a metallic or metal-ceramic alloy.

7. An element (1) according to any preceding Claim, characterised by the fact that the said wear-protection layer (4) is obtained by means of a gaseous nitriding process at a temperature equal to or less than 500°C.

8. An element (1) according to any preceding Claim, characterised by the fact that it comprises a piston ring for a high speed diesel engine.

9. A process for forming a wear-protection layer (4) over a sliding surface (2,2a) of an element (1) constituting a component of the combustion chamber of a diesel engine, which can be worn away during the running-in period of the engine, characterised by the fact that it comprises a gaseous nitriding phase of the said surface (2,2a) performed with ammonia at a temperature less than 500°C in conditions such as to obtain on the said surface (2,2a) the formation of a nitride layer substantially of ε type.

10. A process according to Claim 9, characterised by the fact that the said nitriding phase is performed at an absolute pressure lying between one and ten Torr and by applying a potential difference between the said element (1), held at cathodic potential, and a wall of a nitriding oven within which the said nit-

riding phase is performed, maintained at anodic potential equal to or greater than about 350 volts.

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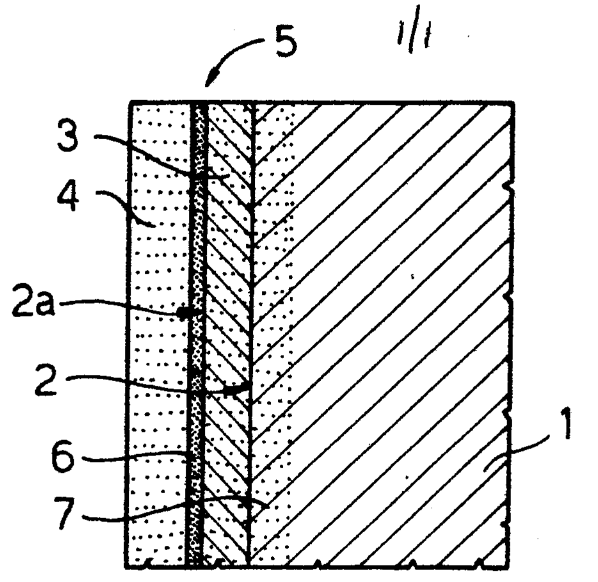

Fig.1

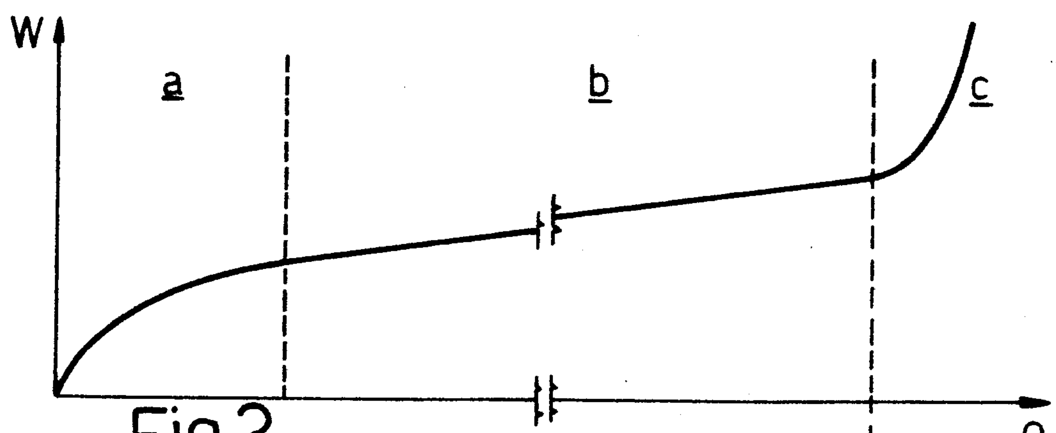

Fig.2

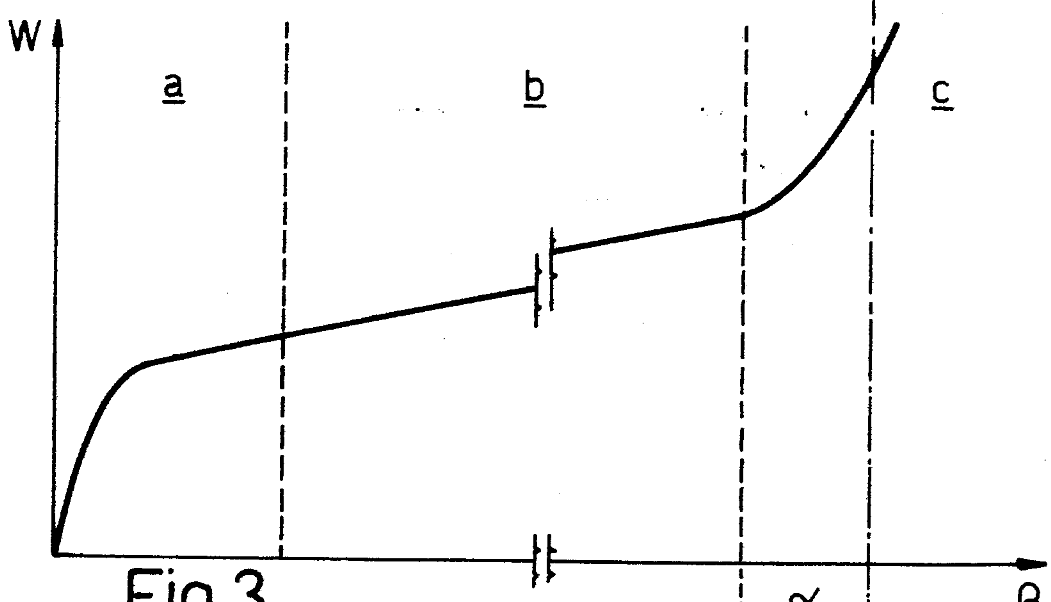

Fig.3