

(19)



(11)

**EP 3 159 427 A1**

(12)

**EUROPEAN PATENT APPLICATION**

(43) Date of publication:  
**26.04.2017 Bulletin 2017/17**

(51) Int Cl.:  
**C23C 8/26** (2006.01)      **C23C 8/34** (2006.01)  
**C23C 8/80** (2006.01)      **C23C 28/04** (2006.01)  
**F01L 3/04** (2006.01)

(21) Application number: **16192608.4**

(22) Date of filing: **06.10.2016**

(84) Designated Contracting States:  
**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR**  
 Designated Extension States:  
**BA ME**  
 Designated Validation States:  
**MA MD**

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(30) Priority: **08.10.2015 BR 102015025727**

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(54) **VALVE FOR INTERNAL COMBUSTION ENGINES**

(57) The present invention relates to a valve (1) for internal combustion engines wherein at least one region of the valve (1) comprises a nitrided layer (10) formed by a solid solution of nitrogen provided within the metallic matrix of the substrate (8) of the valve (1), the nitrided

layer (10) being obtained by means of a heat treatment with diffusion of nitrogen, the nitrided layer (10) being provided with high hardness, conferring excellent wear resistance, in addition to high corrosion resistance, combining different properties in the valve (1).

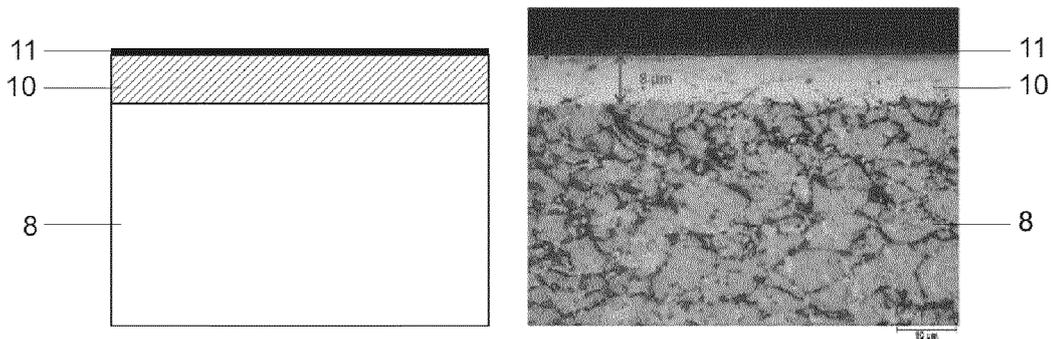


Fig. 2

**EP 3 159 427 A1**

## Description

**[0001]** The present invention relates to a valve for use in internal combustion engines wherein at least one region of the valve comprises a nitrided layer formed by up to 10 % by weight of nitrogen in solid solution provided in the metallic matrix of the valve, conferring excellent wear resistance, in addition to high corrosion resistance.

### Description of the State of the Art

**[0002]** The valves for use in internal combustion engines are high precision components submitted to high thermal and mechanical stresses. They are housed in the head(s) of the engine for the purpose of undertaking different tasks, such as perfectly and sealing areas of flow, controlling the exchange of gases, and sealing the cylinders from the exterior, in addition to dissipating the heat absorbed from the gases resulting from combustion, transferring it to a valve seat ring and to a valve guide.

**[0003]** The valves are divided into inlet, controlling the intake of gaseous mixture into the cylinder of the engine, and exhaust, permitting the escape of the gases following the explosion. There is a generic difference between inlet and exhaust valves such that the inlet valves, cooled by the unburnt gases, need to resist high mechanical stresses, particularly in the contact thereof with the valve seat.

**[0004]** The exhaust valves, in addition to great mechanical demands, also need to resist high thermal stresses and chemical corrosion. Furthermore, they work under temperatures ranging around 800 °C, opening and closing approximately 70 times per second, and are subjected to an average of 300 million load alternations.

**[0005]** By virtue of the different stresses whereto a valve is subjected, the constructional configuration thereof is, in general, very similar. Consequently, as may be observed in figure 1, a valve is constituted by a head in disc form comprising a seating region and a neck region acting as transitional region to the stem, whilst at the extremity of the stem opposite to the head the tip of the valve is located. Moreover, in the region of the stem, adjacent to the tip of the valve, one or more neckings may be observed forming the grooves of the valve. Each region of the valve is submitted to different working conditions, being stressed as a consequence in a different manner.

**[0006]** In summary, the valves must be resistant to three different types of stress, mechanical, thermal and chemical. In relation to the mechanical strength, the valves must present resistance to impacts in the seating region and in the region of the tip. In terms of wear resistance, the principal parts affected are the seating region, the stem and the tip of the valve. In turn, resistance to pressure must be a characteristic of the face of the head. Finally fatigue strength is necessary by virtue of the constant alternation between the tensile and compression stresses.

**[0007]** The requirement for thermal resistance arises

from the temperature of combustion, from the high temperatures of the exhaust gases and from the fatigue caused by the alternation between high and low temperatures. Furthermore, chemical resistance is necessary to prevent the facility of corrosion in the corrosive environment of the gases, humidity and working temperatures to which the valve is subject.

**[0008]** Current engines are, increasingly, stressed under extreme conditions, whether at high temperatures and/or speeds, the objective being to increase the fuel efficiency thereof and deliver greater power. As a consequence of these new stresses, the components of the engines, in particular the valves, present successive modifications, always with the objective of increasing the working life of these elements.

**[0009]** In this manner, having the objective of overcoming the demanding working conditions whereto the valves are subjected, it is very common that the valves are monometallic of special alloys, bimetallic, or that they be provided with inserts.

**[0010]** The monometallic valves are constructed of a single material and are applied in parts experiencing moderate demand. On the other hand, the bimetallic valves are applied in situations of greater demand, a specific material being applied for each part of the valve. Naturally, these valves have a higher cost by virtue of the manufacturing process thereof, presenting limitations and, consequently, not being justifiable for a great proportion of the applications.

**[0011]** Up to the present time, among the most common solutions of coating engine valves in the state of the art is nitridation, conferring high hardness upon the surface of the valve by virtue of the formation of hard phases of nitrides/carbides, with the consequent increase of the wear strength thereof.

**[0012]** However, nitridation also presents a great disadvantage in the sense that it diminishes the corrosion resistance of the valves. There exist two principal mechanisms inherent to the nitridation responsible for rendering the valves susceptible to corrosion:

**[0013]** Depassivation: all the stainless steels, principal material of manufacture of the valves, comprise a film of oxide ( $\text{Cr}_2\text{O}_3$ ), "passive" and rich in chromium, formed naturally upon the surface of the steel. In spite of the film having an insignificant thickness (from 1 to 5 nanometres), it is extremely adherent and chemically stable. The process of nitridation ruptures the passive film in order to render possible the diffusion of the nitrogen into the structure. This rupture of the passive film signifies that the steel loses its anticorrosive properties, in this manner diminishing the corrosion resistance of the material.

**[0014]** Chromium depletion: the process of nitridation causes the depletion of the chromium of the solid solution comprised within the matrix of the steel, by virtue of the formation and precipitation of chromium nitrides. The chromium nitrides "rob" the chromium from the metallic matrix causing the diminution of the corrosion resistance of the nitrided surface, and may render the use of the

steel unviable in many applications.

**[0015]** In this respect, in spite of the nitridation process conferring high wear resistance on the valve, this also drastically lowers the corrosion resistance of the stainless steels, leaving the valves susceptible to corrosion in acidic environments.

**[0016]** Whilst diverse attempts exist which endeavour to minimise the wear to which the valves are subject, the solutions of the state of the art do not offer an engine valve achieving, concomitantly, a superior performance in the matter of wear resistance and corrosion resistance.

**[0017]** It is consequently necessary to obtain a valve for internal combustion engines receiving a heat treatment with diffusion of nitrogen in solid solution provided in the metallic matrix of the valve, conferring excellent wear strength and high corrosion resistance.

#### Objects of the Invention

**[0018]** A first object of the present invention is the provision of a valve for use in internal combustion engines receiving a heat treatment with diffusion of nitrogen in solid solution provided in a metallic matrix.

**[0019]** The present invention furthermore has as object the provision of a valve provided with a nitrided layer comprising between 3 and 50 micrometres, having a hardness exceeding 900 HV in at least one region of the valve.

**[0020]** Finally, the present invention has as object the provision of a valve presenting excellent wear resistance in general, in addition to high corrosion resistance, combining different properties in the valve.

#### Brief Description of the Invention

**[0021]** The objects of the present invention are achieved by a valve for internal combustion engines provided with a ferrous body or substrate comprising chromium, such that at least one region of the valve comprises a nitrided layer formed by up to 10 % by weight of nitrogen in solid solution provided in the metallic matrix of the substrate of the valve, the nitrided layer presenting a gradual transition of the percentage by weight of nitrogen, wherein the outermost portion of the nitrided layer presents 10 % by weight of nitrogen decreasing gradually until reaching the substrate of the valve, the nitrided layer comprising a thickness of between 3 and 50 micrometres and hardness exceeding 900 HV.

**[0022]** The objects are furthermore achieved by a valve comprising a nitrided layer provided upon all the surfaces thereof, being preferentially an inlet valve.

#### Brief Description of the Figures

**[0023]** The present invention will, hereinafter, be described in greater detail on the basis of an example of embodiment represented in the figures. The figures show:

Figure 1: schematic lateral view of a valve with all the parts constituting it;

Figure 2: schematic drawing and photograph of the nitrided layer provided upon the valve of the present invention;

Figure 3: photographs showing the difference in depth of corrosion between a valve of the state of the art and of the present invention in a first corrosion test;

Figure 4: graphic representation of the difference in depth of corrosion between valves of the state of the art and of the present invention for the first corrosion test;

Figure 5: photographs showing the difference in depth of corrosion between a valve of the state of the art and of the present invention in a second corrosion test; and

Figure 6: graphic representation of the difference in depth of corrosion between valves of the state of the art and of the present invention for the second corrosion test.

#### Detailed Description of the Figures

**[0024]** The present invention relates to a valve 1 for internal combustion engines wherein at least one region of the valve 1 comprises a nitrided layer 10 formed by a solid solution of nitrogen provided in the metallic matrix of the substrate 8 of the valve 1, the nitrided layer 10 being obtained by means of a heat treatment with diffusion of nitrogen, comprising high hardness, conferring upon the valve 1 excellent wear resistance in addition to high corrosion resistance, combining different properties in the valve 1.

**[0025]** As aforementioned, the valves 1 for use in internal combustion engines are components of high precision, housed in the head of the engine, responsible for different tasks and subjected to high thermal and mechanical stresses.

**[0026]** By virtue of these different loads and stresses to which the valve 1 is submitted, the constructional configuration thereof is, in general, very similar. Consequently, as may be observed in figure 1, a valve 1 is constituted of a head 2 in the form of a disc comprising a seating region 3 and a neck region 4 acting as region of transition to the stem 5, whilst at the extremity of the stem 5 opposite to the head 2 there is located the tip 6 of the valve 1. Moreover, in the region of the stem 5, adjacent to the tip 6 of the valve 1, one or more neckings may be observed forming the grooves 7 of the valve 1.

**[0027]** Among the materials utilised in the manufacture of the valves 1 for internal combustion engines are, preferentially, the austenitic and martensitic stainless steels

characterised by presenting excellent properties of corrosion resistance, having however low surface hardness and, consequently, low wear resistance.

**[0028]** In this respect, the processes of hardening by nitridation are commonly applied, increasing the surface hardness, however significantly prejudicing the corrosion resistance of the material by virtue of the intense precipitation of nitrides and carbides which impoverish the matrix of chromium.

**[0029]** The process of nitridation consists, basically, in the addition of nitrogen, in the atomic form thereof, upon the surface of a metal, usually steel. The nitrogen tends to occupy the interstices of the crystalline structure, migrating by diffusion into the interior of the metal. Traditionally, the processes of nitridation applied to stainless steels utilise temperatures in the band between 500 °C and 600 °C in salt baths or are carried out under a reductive nitriding atmosphere obtained from the dissociation of ammonia gas.

**[0030]** Differing from the valves traditionally obtained through nitridation processes, the valve 1 of the present invention comprises a nitrided layer 10 formed by solid solution having a very high concentration of nitrogen provided within the metallic matrix of the valve 1, without the formation of the aforementioned undesirable nitrides. Figure 2 presents the structure of the nitrided layer 10 of the valve 1 of the present invention. The metallographic test carried out revealed a nitrided layer of 8 micrometres devoid of the presence of nitrides.

**[0031]** The heat treatment utilised comprises low-temperature diffusion of the nitrogen, providing the hardening of the surface together with a method of depassivation which does not destroy the film of chromium oxide. In figure 2 the film of oxide 11 formed upon the nitrided layer 10 may be observed. In this manner there is formed upon the surface a new phase, a supersaturated and metastable solid solution of high hardness without the diminution of the corrosion resistance inherent to the stainless steels. The heat treatment with diffusion of nitrogen causes a modification to the surfaces of the valve 1, transforming the structure of the substrate 8.

**[0032]** The nitrided layer 10 presents a gradual transition, or a gradient, of percentage by weight of nitrogen contained in solid solution, comprising up to 10 % by weight of nitrogen in an outermost portion of the nitrided layer 10 and decreasing gradually until reaching the substrate 8 of the valve 1. In the same manner, the nitrided layer 10 presents a gradient of hardness comprising a hardness of up to 2000 HV in the outermost portion of the nitrided layer and gradually decreasing. Preferentially, the nitrided layer 10 comprises a hardness exceeding 900 HV.

**[0033]** In this sense, the present invention presents a valve 1 for internal combustion engines, particularly a valve 1 provided with a ferrous body wherein at least one region of the valve 1 comprises a nitrided layer 10, having the objective, principally, of increasing the wear resistance thereof together with increased corrosion resist-

ance.

**[0034]** The valve 1 which is the object of the present invention has as innovation the fact that received upon at least one of the parts thereof is a nitrided layer 10 comprising nitrogen in a solid solution provided within the metallic matrix of the material. The nitrided layer 10 is provided upon the totality of the ferrous body or substrate 8 of the valve 1, provided with high hardness, not revealed by any document of the prior art, and confers upon the valve 1 excellent wear resistance in addition to high corrosion resistance.

**[0035]** Moreover, according to the preferential embodiment, the nitrided layer 10 is provided with a thickness of between 3 and 50 micrometres, preferentially provided with a thickness of between 3 and 35 micrometres, being obtained by a heat treatment rendering possible the addition of nitrogen in solid solution, in this manner there being obtained a nitrided layer 10 of high hardness, without prejudicing the anticorrosive properties inherent to stainless steels.

**[0036]** In a preferable embodiment, the heat treatment for diffusion of nitrogen is realised at a temperature of less than 450 °C, having a period of duration of the process of 3 to 20 hours. The nitrided layer 10 is obtained by the reaction of the atmosphere rich in nitrogen with the metallic matrix of the substrate 8, preventing the formation of nitrides.

**[0037]** Figures 3 to 6 present results of corrosion tests realised upon the valve 1 of the present invention. Two types of corrosion test were carried out, the first test being conducted by the Moneypenny Strauss method wherein the test piece of the valve 1 is immersed in a solution of pentahydrated copper and sulphuric acid ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ). The results of the first corrosion test are presented in figures 3 and 4 wherein there are compared three possibilities of materials for the valves applied in internal combustion engines:

- 1) State of the Art 1: stainless steel, austenitic or martensitic, without any surface hardness treatment;
- 2) State of the Art 2: stainless steel, austenitic or martensitic, submitted to a conventional process of hardening by nitridation;
- 3) Present Invention: stainless steel, austenitic or martensitic, subjected to the process of hardening by nitridation utilised in the present invention.

**[0038]** Figure 3 presents two photographs showing the depth of intergranular corrosion following the implementation of the first test. As may be observed, the valve having conventional nitridation (state of the art) presents intergranular corrosion of up to 500 micrometres whilst the valve of the present invention presents corrosion of less than 300 micrometres. The areas of corrosion are represented by the whitish bands apparent in the photographs.

**[0039]** Figure 4 represents graphically the results of the first corrosion test carried out. It may be observed

that the valve not subjected to any process of hardening (state of the art 1) presents very low levels of corrosion, having a corrosion depth of 100 micrometres. It is important that it be recalled that those valves without heat treatment present high corrosion resistance, but low hardness and wear resistance. The valve subjected to the conventional process of nitridation presented high corrosion, having a depth of 500 micrometres. In contrast, the valve of the present invention, presenting a hardness exceeding 900 HV and high wear resistance, also presented high corrosion resistance, having a depth of less than 300 micrometres. Consequently, the valve of the present invention presents a depth of corrosion at least 40 % less than that presented by the valve subjected to the conventional nitridation.

**[0040]** Figure 5 presents two photographs showing the depth of corrosion following the implementation of a second corrosion test using method VDA 230-214 for metallic materials applied upon components subjected to the exhaust gases of the engine. It may be observed that the valve having conventional nitridation (state of the art) presents a visible band of corrosion having a depth exceeding 20 micrometres. In contrast, the valve of the present invention presents a minimal band of corrosion having a depth of less than 3 micrometres. These values of depth of corrosion are represented graphically in figure 6.

**[0041]** It is important that it be noted that the results of the second corrosion test carried out show that the valve 1 of the present invention presents a depth of corrosion 85 % less than the valve of the state of the art.

**[0042]** Consequently, both the corrosion tests carried out clearly demonstrate an improvement in the corrosion resistance of the valves of the present invention in relation to the valves subjected to the conventional nitridation.

**[0043]** In summary, the valve 1 which is the object of the present invention presents a series of advantages and benefits in relation to the valves presently known, these being:

- I. Nitrided layer having high hardness, exceeding 900 HV, up to 2000 HV;
- II. Excellent wear resistance in combination with high corrosion resistance;
- III. Maintenance of the passive film of oxide 11 of the material by virtue of the low temperature of diffusion of nitrogen in the solid solution into the metallic matrix of the substrate 8 of valve 1.

**[0044]** An example of a preferred embodiment having been described, it shall be understood that the scope of the present invention covers other possible variations being limited solely by the content of the appended claims, therein included the possible equivalents.

## Claims

1. Valve for internal combustion engines provided with a ferrous body or substrate (8) comprising chromium, **characterised in that** at least one region of the valve (1) comprises a nitrided layer (10) formed by up to 10 % by weight of nitrogen in a solid solution provided within the metallic matrix of the substrate (8) of the valve (1).
2. Valve according to Claim 1, **characterised in that** the nitrided layer (10) presents a gradual transition of the percentage by weight of nitrogen, wherein the outermost portion of the nitrided layer (10) presents 10 % by weight of nitrogen decreasing gradually until reaching the substrate (8) of the valve (1).
3. Valve according to Claim 1, **characterised in that** it comprises a film of oxide (11) upon the nitrided layer (10).
4. Valve according to Claim 1, **characterised in that** the nitrided layer (10) comprises a thickness varying between 3 micrometres and 50 micrometres.
5. Valve according to Claim 1, **characterised in that** the nitrided layer (10) comprises a surface hardness exceeding 900 HV.
6. Valve according to Claim 1, **characterised in that** the nitrided layer (10) is provided upon all the surfaces of the valve (1).
7. Valve according to Claim 1, **characterised in that** it is an inlet valve (1).

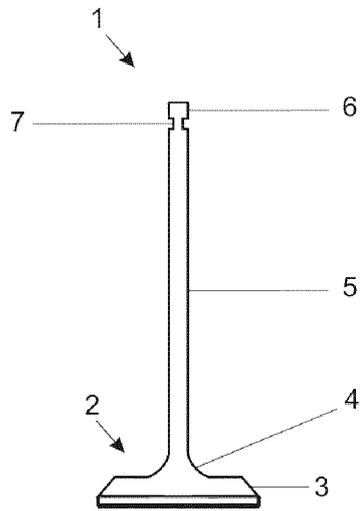


Fig. 1

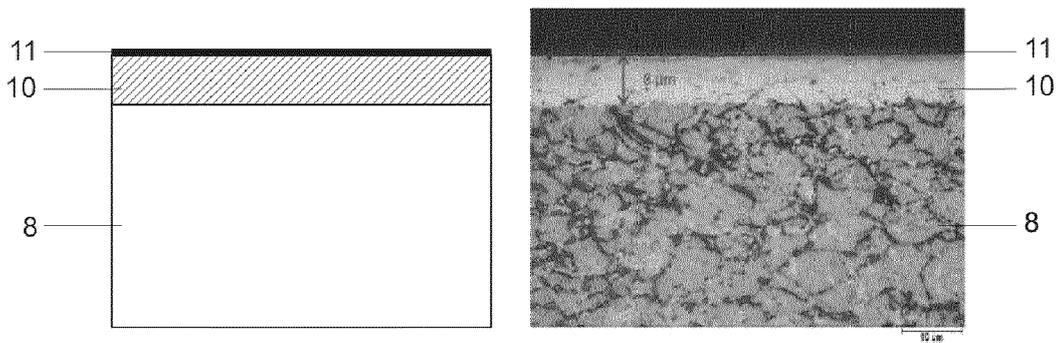


Fig. 2

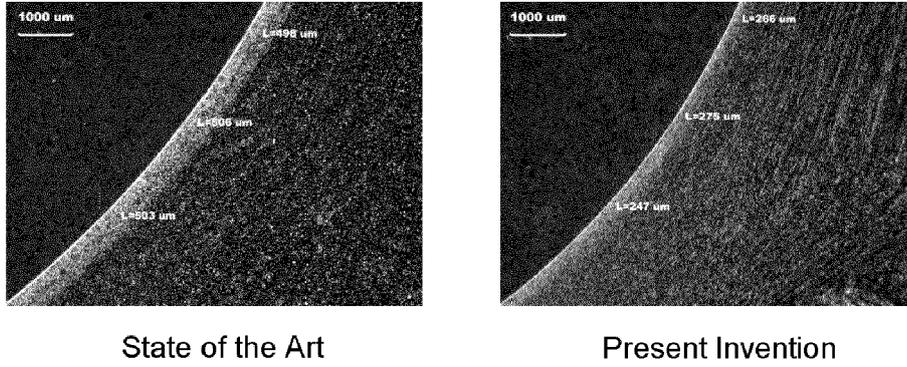


Fig. 3

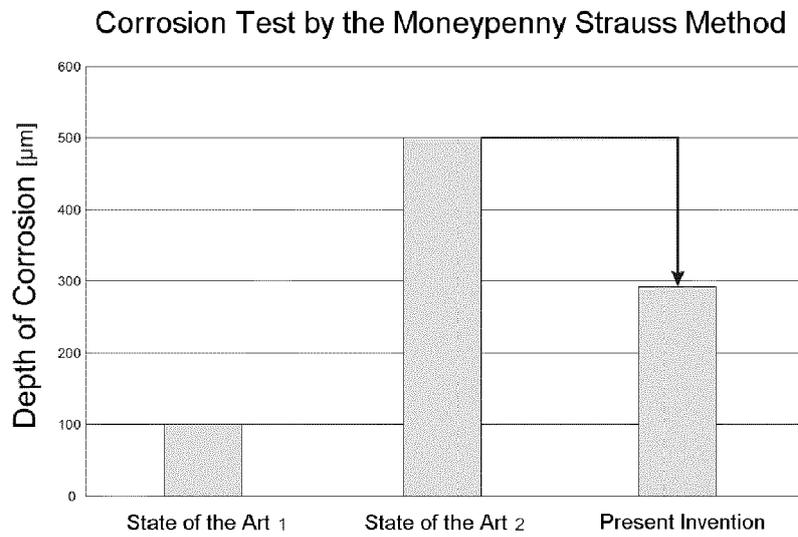


Fig. 4

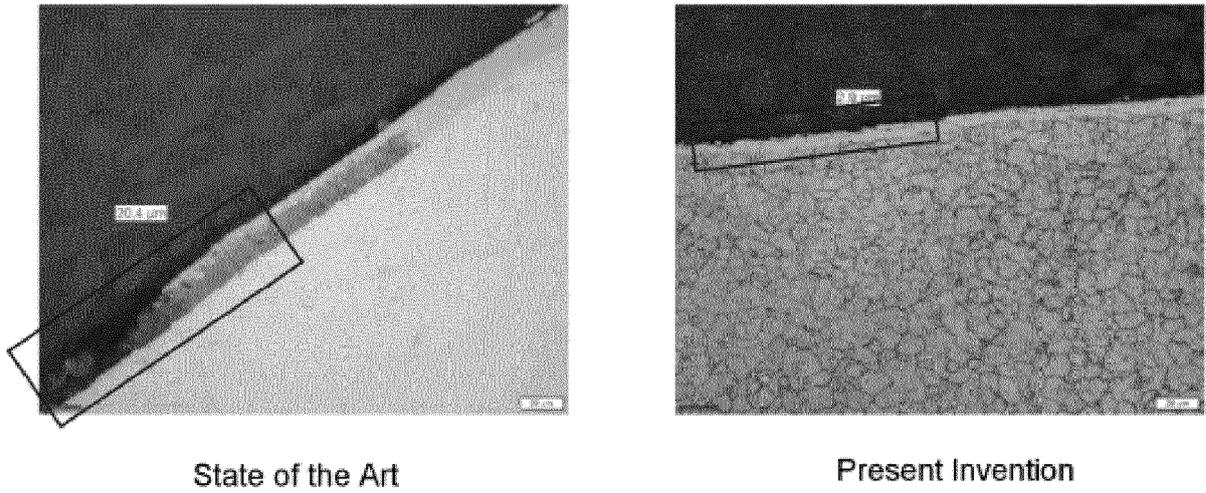


Fig. 5

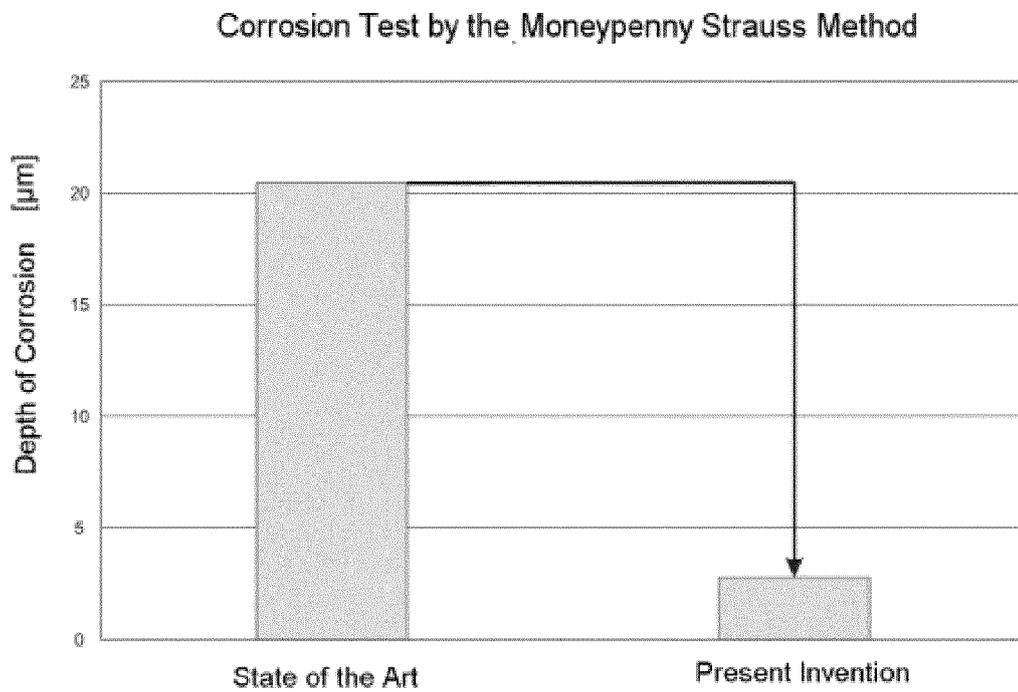


Fig. 6



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Application Number  
EP 16 19 2608

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Y	* page 5 - page 9; claims 1, 3, 4, 5;	1,4-7	
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CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

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ANNEX TO THE EUROPEAN SEARCH REPORT  
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5 This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.  
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