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# (54) Self-healing layer on non-ferrous metals using polyoxometalates

(57) The invention relates to a method for applying a multifunctional layer on a substrate. Accordingly said layer is applied by means of a process by using an aqueous solution that comprises a POM and/or a crack-healing agent, which POM and/or a crack healing agent is/are incorporated in said layer during said process to obtain a self-healing layer. Generally, said substrate comprises a metallic substrate, preferably a non-ferrous metallic substrate, and most preferably Al, Mg, Ti and alloys thereof. Said POMs are heteropolyanions of the type $(X_n\text{-}M_mO_y)^{x-}$, in which X=Si, P, Ce, B, Mn and in which M=Mo, W or V and $y>1$, $m>1$ and $n \leq m$ and x indicates the valence of the polyanion. A Keggin-type POM is preferred. Said crack-healing agent is selected from particles of mixed oxides, clay particles, metallic oxide/epoxy resin microspheres, or a mixture thereof. Preferably said POMs are supported by media selected from insoluble micro- or nanoparticles (e.g. $SiO_2$) or polymer capsules. The application of said layer occurs by means of conventional anodising, hard anodising, plasma electrolytic oxidation, or electro(less) deposition. Further the invention relates to said POM and/or a crack-healing agent. Finally, the present invention relates to a coated substrate, obtained by the method according to the invention.

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## Description

**[0001]** The present invention relates to a method for applying a multifunctional layer on a substrate. The invention also relates to an aqueous solution comprising a polyoxometalate (POM) and/or a crack-healing agent. The invention further relates to a coated non-ferrous substrate, preferably a coated non-ferrous metallic substrate obtained by the method according to the invention.

**[0002]** Methods to produce multifunctional layers (i.e. layers with at least two engineering properties) are known in the state of the art and include hard anodising (HA), plasma electrolytic oxidation (PEO), electro(less)deposition. The layers obtained are amorphous/crystalline oxides (HA/PEO) or metallic layers (electro(less)deposition) and have very good properties of hardness, wear (abrasive and adhesive), non-stick properties, etc. Extra treatment steps are often applied to further enhance the corrosion resistance or lubrication properties. For example, a method to apply a multifunctional layer is known from US patent 3622473. In this patent, a process is described for anodic oxidation of aluminium in an electrolyte to produce a durable oxide film thereon from 1-20 μm, followed by application of a resin coating by electrodeposition and curing of this resin coating.

**[0003]** A disadvantage of the method of the state of the art is that in case of cracking of the resulting multifunctional layer, the underlying metal substrate may become exposed to the outer environment, in this way leading to local corrosion. This can be catastrophic for the product as is the case of coated magnesium alloys when severe galvanic corrosion occurs. Another disadvantage of the method of the state of the art is that in case of a crack of the resulting layer, this cannot be healed and remains as a weak area in the layer. The layers mentioned above from the state of the art are prone to cracking due to their brittleness, internal stresses, different coefficient of thermal expansion relative to the substrate, service conditions.

**[0004]** The aim of the invention is to provide a method for applying a multifunctional layer on a substrate that overcomes at least one of the problems mentioned above. This aim is reached by a method according to claim 1. This method is characterised in that the layer is applied by means of a process by using an aqueous solution that comprises a POM and/or a crack-healing agent, which POM and/or a crack healing agent is/are incorporated in said layer during said process to obtain a self-healing layer.

**[0005]** The invention proposes the incorporation of two types of healing agents during layer growth/deposition. For corrosion, POMs are proposed as healing agents. For cracking, several types of crack-healing agents are provided. According to the invention, protecting layers can result that comprise only POMs or only crack-healing agent or both POMs and crack-healing agents as healing agents.

**[0006]** POMs represent a distinct class of complex metal oxygen anions with general formulae $[M_mO_y]^{p-}$ or $[X_nM_mO_y]^{x-}$ ($n \leq m$, m and n >1) in which M (addenda atom) is a transition metal from the group Mo, V, W, and more rarely Nb, Ta in their highest oxidation state (the highest valence) and the heteroatom X can be almost any element from the periodic table except the rare gases.

**[0007]** These POM-complexes have a series of attractive properties that make them suitable for numerous applications such as catalysis, medicine, sensors, dopants, dyes/pigments, separations, clinical analysis, food chemistry, waste degradation, etc. These properties include: high stability of their redox states, adsorption ability on solid surfaces, multiple redox reactions without major changes in their structure, tunability of their redox potential by changing the heteroions and/or addenda ions without affecting their structure, multiple electron transfer, fully oxidized compounds, large size, non-toxic properties, etc.

**[0008]** The use of POMs for protecting a metal layer is known from the state of the art (Frontiers in Bioscience 9, 1759-1770, May 1, 2004, p1792). However, in the state of the art POMs are used as coatings *per se* on metallic substrates. The coatings are produced by immersion of the substrate in aqueous solutions containing POMs (i.e. chemical conversion coatings). According to the invention, the POMs are incorporated in a layer during layer growth/deposition.

**[0009]** In a preferred embodiment of the invention, the method according to claim 1 is characterised in that said substrate comprises a metallic substrate, more preferred, a non-ferrous metallic substrate. Metallic substrates are commonly used in the fields of application of the present invention. Examples of the non-ferrous metal forming the substrate are Al, Mg, and Ti and the alloys thereof. Depending on the process used for layer growth/deposition, other metals can also be included. For example, in the process of electroless and electrodeposition, as described below, also Fe, Cu and their alloys can be used.

**[0010]** As will be more substantiated below, the type of aqueous solution in the present invention depends on the process used for layer growth/deposition, i.e. it can be either an anodizing electrolyte (HA/PEO), an electroless solution or the electrolyte used in the electrodeposition process.

**[0011]** According to the present invention, a method is provided in which the POMs in the aqueous solution are heteropolyanions of the type $[X_nM_mO_y]^{x-}$ in which X = Si, P, Ce, B, Mn and M = Mo, W, V and in which $y > 1$, $m > 1$ and $n \leq m$. Examples of POMs include $(SiMo_{12}O_{40})^{4-}$, $(CeMo_{12}O_{42})^{8-}$, $(SiW_{12}O_{40})^{4-}$, $(PW_{12}O_{40})^{3-}$. However, the POMs to be incorporated in the layers are not limited to these mentioned above and other POMs or combinations thereof may also be included. Use of the POMs in the method according to the invention provides a stable layer. It provides excellent corrosion protection, as known in the state of the art.

**[0012]** In a preferred embodiment, the POM is $(XM_{12}O_{40})^{x-}$. These are called Keggin-type POMs and represent the most studied and important class of POMs due to their high (thermal) stability and availability.

**[0013]** The trigger for POMs to react is the presence of (hydrothermal) corrosive environments (e.g. presence of $Cl^-$, $SO_4^{2-}$). The mechanism involves the ability of the POM to accept electrons from the corrosive ions, in this way inactivating these ions before reaching the underlying substrate. The valence of the transition metal present in the POM decreases, e.g. from VI to V, IV or III. However, the reduced form of POM can be oxidized in air to regenerate the initial state, the highest oxidation state, without changing its structure. In this way, a multiple self-healing effect is ensured. This multiple self-healing effect involves that the POM can react again for more successive times.

**[0014]** The present invention proposes that in addition to POM, crack-healing agents are included in the layers. These have the possibility to fill-in the local cracks or defects that might appear during the service life of the product. Thereto also crack-healing agents have to be present in the solution according to the invention. The trigger to initiate crack healing is the appearance of a crack in the presence or absence of a hydrothermal environment. In the presence of a hydrothermal environment, the healing agent undergoes chemical or physical reactions with formation of new products with increased volume. In the absence of a hydrothermal environment they can fill-in the crack being released and fixed at the crack location.

**[0015]** According to the present invention, a method is provided that is characterised in that the crack-healing agent is selected from the group of particles of mixed oxides, clay particles, metallic oxide/epoxy resin microspheres or a mixture thereof. The invention is however not limited to these crack-healing agents. Examples of mixed oxides are $CaO \cdot Al_2O_3$ or $CaO \cdot 2Al_2O_3$. Advantages of metallic oxides like Al and Ca oxides is that under hydrothermal conditions they undergo chemical reactions to form products with increased volume, like $AlH(OH)_4$ or $\gamma$-AlOOH. Clay particles are advantageous for their good swelling properties, when contacted with hydrating environments, in this way filling-in the cavities/cracks and providing a barrier for the passage of ions inside the cavities/cracks. An example of clay particles is hectorite. Hectorite is described as a good swelling agent, in which swelling properties are provided by the layered structure of the material containing cations that become hydrated in the interlayer space. In the absence of a hydrothermal environment, the third crack-healing agent proposed can fill-in the crack by the metallic oxide particles being freed during cracking of the microspheres and bound to the layer by the drying epoxy resin. An advantage is that this embodiment can be used in dry, non-hydrating environments.

**[0016]** The crack-healing characteristics of the three alternative agents described are functional at temperatures between room temperature (25°C) and circa 200°C.

**[0017]** The conditions for incorporation of self-healing agents can be adjusted to create a tailored, i.e. uniform or gradient, distribution of the healing agents through the layer depending on the layer type and application (i.e. susceptibility to cracking and corrosion).

**[0018]** Therefore, according to the invention, the POMs and crack-healing agents can be present in the solution in several states. The POMs can for example be distributed in a free state. In this state POMs are present in the solution as unsupported anions.

**[0019]** In another embodiment the POMs are present in a supported or immobilised state. In this form, the POMs are carried by media. According to the invention, POMs can be carried by particles like microparticles or nanoparticles, e.g. $SiO_2$, to form clusters. $SiO_2$ provides a good adsorbance for POMs and therefore shows a good storage capacity of POMs. In this way the concentration of POM in the layer can be increased. In another embodiment, the POMs can be encapsulated in polymer capsules. This would be advantageous when electrolytes are used in which POMs are not stable. Examples of polymers suitable for encapsulation known from the state of the art include the urea-formaldehyde based polymers.

**[0020]** In a separate embodiment of the invention, the particles carrying the POMs are the crack-healing particles. The advantage of this situation is that 1) both the POMs and the crack healing agent are present on the same location, 2) a higher storage capacity is reached for the POM, 3) the particles become better dispersed in the solution because the negatively charged POMs reject each other and 4) the crack-healing agent is protected from direct contact with solution thus being preserved in the layer.

**[0021]** The crack-healing agents can be also encapsulated in microspheres. The main purpose is that they are preserved in a dry condition required for the crack healing effect. As described above, the crack-healing agent can comprise metallic oxide particles and an epoxy resin encapsulated in polymer microspheres.

**[0022]** Combinations of POMs and crack-healing agents according to one of the states described above are also incorporated in the invention.

**[0023]** As described above, according to the invention, the substrate is protected by formation of an oxide or metallic protecting layer comprising at least the POMs and/or the crack-healing agent. According to preferred embodiments of the invention, the layers containing POMs and/or crack-healing agent can be deposited/grown on the substrate via the following processes: conventional anodising, hard anodising, plasma electrolytic oxidation and electro(less) deposition.

**[0024]** In anodising, the non-ferrous metallic substrate to be covered by the protecting layer (i.e. Al, Mg, Ti and alloys thereof) is made anode in an electrolytic cell. In this way the surface is oxidised under the electric field using appropriate electrolytes known in the state of the art. During formation of the layer (amorphous oxides), POMs are incorporated in the layer by electrophoresis or adsorption. The microspheres comprising the crack-healing agent are entrapped during formation of the layer. As known by a person skilled in the art, hard anodising of aluminium alloys results in a more dense layer that is less porous and has better wear resistance than a layer obtained by conventional anodising. Both processes may use a similar electrolyte. However, hard anodising is performed at ca. 0°C whereas conventional anodising is performed at room temperature. The current density for conventional anodizing is usually between 1-2 A/dm$^2$, whereas for hard anodizing this can be higher, preferably between 2-4 A/dm$^2$. Therefore, using hard anodising, thicker layers can be obtained.

**[0025]** During PEO, anodic oxidation under sparking (plasma discharges) occurs on the surface of the substrate made anode in the electrolytic cell. PEO has the advantage that more types of ions/phases can be incorporated in the layer. The resulting layer is a crystalline oxide, which has a very high hardness (e.g. 2000 HV vs 600 HV in hard anodising). During the process of PEO, the POM and/or crack-healing agents are incorporated by electrophoresis or adsorption.

**[0026]** In electro-deposition, the layer is deposited onto the substrate made cathode in an electrolytic cell by reduction of cations under the electric field. The reaction is conducted in acidic pH conditions (e.g. 3.5 - 4 for a nickel Watts bath). The POM and/or crack-healing agents are incorporated by adsorption or electrophoresis.

**[0027]** In electroless deposition processes, the protective layer is formed by chemical reduction of metal cations onto the substrates under appropriate conditions of pH and temperature. As known by a person skilled in the art, chemical, electroless deposition requires a pretreatment to activate the substrate for chemical nickel reduction (e.g. double-zincating in the case of aluminium alloys). The process is performed at about 88°C in an acidic solution (pH preferably between 4.5 and 5). The POM and/or crack-healing agents are incorporated by adsorption and subsequent entrapment in the growing layer.

**[0028]** The POMs and/or the crack-healing agents are distributed throughout the layers including the interface with the substrate and the surface of the layers so that the corrosion inhibition and crack-healing effects can be ensured during the entire life lifetime of the product (under wear conditions or when cracks and damages appear in the layer). All the processes mentioned above for the growth/deposition of layers have the ability to incorporate particles or ions to form the composite or hybrid layers with tailored properties. Oxides and oxide-like properties of the healing agents proposed are compatible with layers structure and their functional properties.

**[0029]** The invention also relates to the aqueous solutions used in the processes of anodising, hard anodising, plasma electrolytic deposition and electro(less) deposition, described above. The essential components for the electrolyte (HA, PEO, electrodeposition) and electroless (electroless deposition) solutions respectively are known to a person skilled in the art. It is clear that these known components can differ for the different requirements of the separate processes, as known in the art. In this way, the aqueous solution as described below can be applied for the methods according to the invention.

**[0030]** According to the invention, an aqueous solution is provided, characterised in that it comprises a POM and/or a crack-healing agent. This solution can be applied advantageously in the methods of the invention.

**[0031]** In a preferred embodiment, in this aqueous solution said POMs are heteropolyanions of the type $(X_n\text{-}M_mO_y)^{x-}$, in which X=Si, P, Ce, B, Mn and in which M=Mo, W or V and $n \leq m$, $m > 1$, $y > 1$, x = the valence of the selected anion. Preferably, said POMs are Keggin $(XM_{12}O_{40})^{x-}$ POMs.

**[0032]** In another preferred embodiment, in the aqueous solution the crack-healing agent is selected from particles of mixed oxides, clay particles, metallic oxide/epoxy resin microspheres or mixtures thereof and that the crack-healing agent can be encapsulated in polymer microspheres.

**[0033]** In a further embodiment of the aqueous solution of the invention, the POMs are supported by media from the group of particles or polymer capsules.

**[0034]** Above described embodiments of the aqueous solution are in particular advantageous for the methods described in this invention. All advantages of these methods also apply to these aqueous solutions.

**[0035]** The invention is further related to a substrate on which a self-healing multifunctional layer is applied via the method of the invention. In a preferred embodiment of the invention, this substrate comprises a metallic substrate, more preferred, a non-ferrous metallic substrate. Metallic substrates are commonly used in the fields of application of the present invention. Examples of the non-ferrous metal forming the substrate are Al, Mg, and Ti and the alloys thereof. Depending on the application process used, also other metals can be used. For example, in the process of electroless and electrodeposition, also Fe, Cu and their alloys can be used.

**[0036]** The multifunctional self-healing layer resulting from the aqueous solution according to claim 1 will have a thickness of larger than 1 up to e.g. 50 μm, depending on the application and the process used. For example, in anodizing, a layer thickness of 20-25 μm is considered optimum for functional properties. The layer according to the invention provides multifunctional properties such as proper hardness, abrasive wear, low friction and non-stick properties at room temperature and higher temperatures (e.g. up to 200°C). By this invention, self-healing properties in case of corrosion and/or cracking are also provided.

**[0037]** For clarification purposes, examples of self-healing layers provided by the present invention are included in Fig. 1. The mode of action of the healing-agents is presented in Fig. 2.

Figure 1 shows three examples of the states in which

POMs and crack healing agents can be distributed in the layers resulting from aqueous solutions according to the invention. Figure la shows dispersed healing agents (POMs) inside the layers deposited *in situ* (i.e. during layer growth) in free, unsupported form. Figure 1b shows the POMs supported by adsorption on particles (e.g. $SiO_2$) to form clusters. Figure 1c shows POMs and crack-healing agents supported by encapsulation.

Figure 2 depicts a non-ferrous metallic substrate on which a layer according to the invention has been deposited. This layer shows a crack. Due to reactions initiated by the change in the environment, POMs stop the process of corrosion and crack-healing agents react to fill-in the crack. In this way, self-healing properties are provided to the multifunctional layer.

## Claims

**1.** A method for applying a multifunctional layer on a substrate, **characterised in that** said layer is applied by means of a process by using an aqueous solution that comprises a POM and/or a crack-healing agent, which POM and/or a crack healing agent is/are incorporated in said layer during said process to obtain a self-healing layer.

**2.** The method according to claim 1, **characterised in that** said substrate comprises a metallic substrate.

**3.** The method according to claim 2, **characterised in that** said metallic substrate comprises a non-ferrous metallic substrate, preferably Al, Mg, Ti and alloys thereof.

**4.** The method according to one of the claims 1 to 3, **characterised in that** said POMs are heteropolyanions of the type $(X_nM_mO_y)^{x-}$, in which X=Si, P, Ce, B, Mn and in which M=Mo, W or V and $y>1$, $m>1$ and $n\leq m$ and x indicates the valence of the polyanion.

**5.** The method according to claim 4, **characterised in that** said POM is a Keggin-type POM.

**6.** The method according to one of the claims 1 to 5, **characterised in that** said crack-healing agent is selected from particles of mixed oxides, clay particles, metallic oxide/epoxy resin microspheres, or a mixture thereof.

**7.** The method according to one of the claims 1 to 6, **characterised in that** said POMs are supported by media selected from insoluble micro- or nanoparticles (e.g. $SiO_2$) or polymer capsules.

**8.** The method according to claim 7, **characterised in that** said particles are crack-healing agent particles.

**9.** The method according to one of the claims 1 to 8, **characterised in that** the crack-healing agent is encapsulated in polymer microspheres.

**10.** The method according to one of the claims 1 to 9, **characterised in that** said process comprises conventional anodising.

**11.** The method according to one of the claims 1 to 9, **characterised in that** said process comprises hard anodising.

**12.** The method according to one of the claims 1 to 9, **characterised in that** said process comprises plasma electrolytic oxidation.

**13.** The method according to one of the claims 1 to 9, **characterised in that** said process comprises electro(less) deposition.

**14.** An aqueous solution **characterised in that** it comprises a POM and/or a crack-healing agent.

**15.** The aqueous solution according to claim 14, **characterised in that** said POMs are heteropolyanions of the type $(X_nM_mO_y)^{x-}$, in which X=Si, P, Ce, B, Mn and in which M=Mo, W or V and $y>1$, $m>1$ and $n\leq m$ and x indicates the valence of the polyanion and said POM is preferably a Keggin-type POM.

**16.** The aqueous solution according to claim 14 or 15, **characterised in that** the crack-healing agent is selected from particles of mixed oxides, clay particles, metallic oxide/epoxy resin microspheres or mixture thereof, and that the crack-healing agent can be encapsulated in polymer microspheres.

**17.** The aqueous solution according to claim 14 to 16, **characterised in that** said POMs are supported by media from the group of particles or polymer capsules, said particles including the particles comprising the crack-healing agent.

**19.** A coated substrate, preferably a metallic substrate, more preferably a non-ferrous metallic substrate, preferably selected from the group of Al, Mg, Ti, obtained by the method according to one of the claims 1-13.

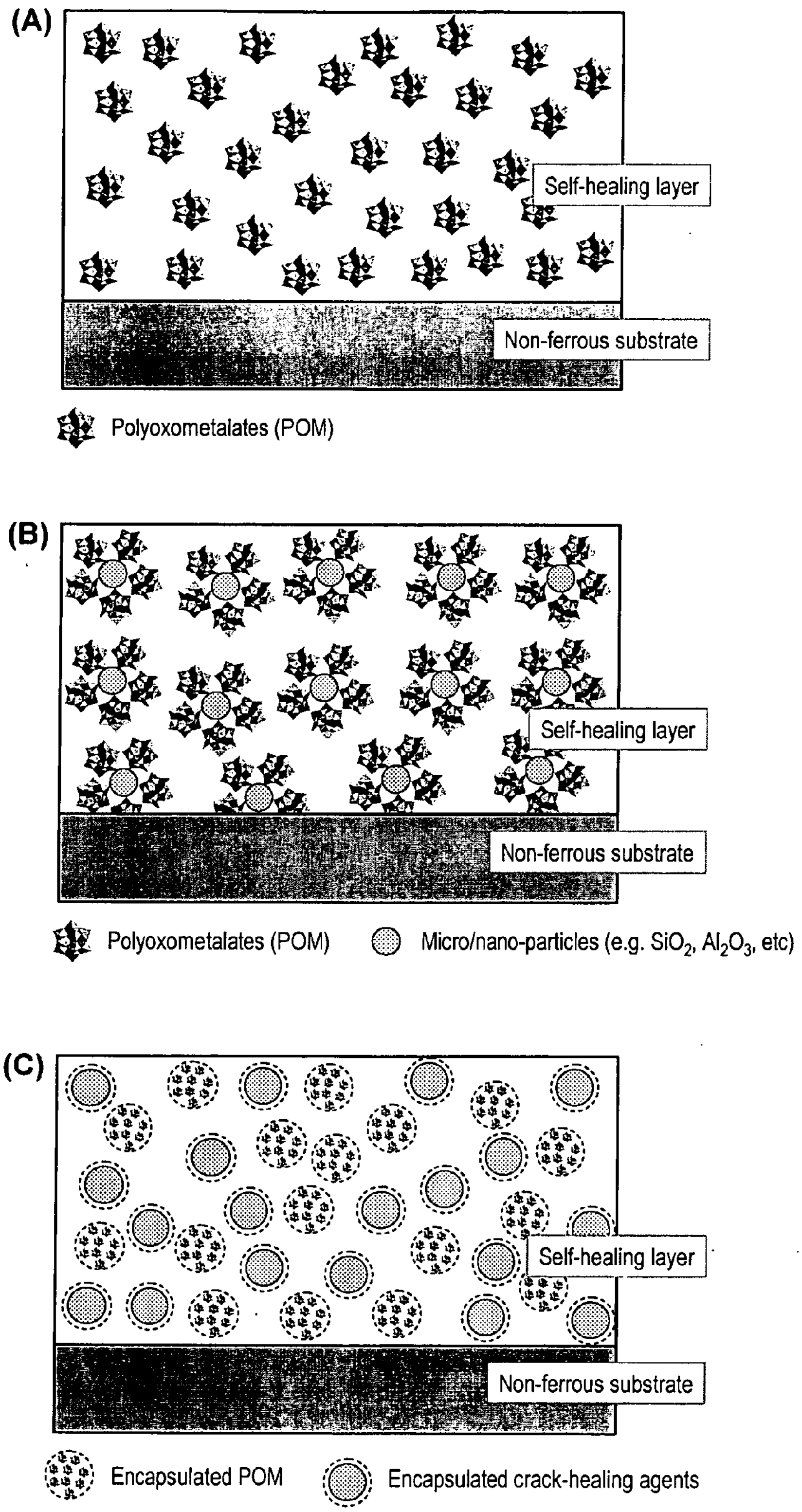
(A)
Self-healing layer
Non-ferrous substrate
Polyoxometalates (POM)
(B)
Self-healing layer
Non-ferrous substrate
Polyoxometalates (POM)
Micro/nano-particles (e.g. $SiO_2$, $Al_2O_3$, etc)
(C)
Self-healing layer
Non-ferrous substrate
Encapsulated POM
Encapsulated crack-healing agents

Figure 1.

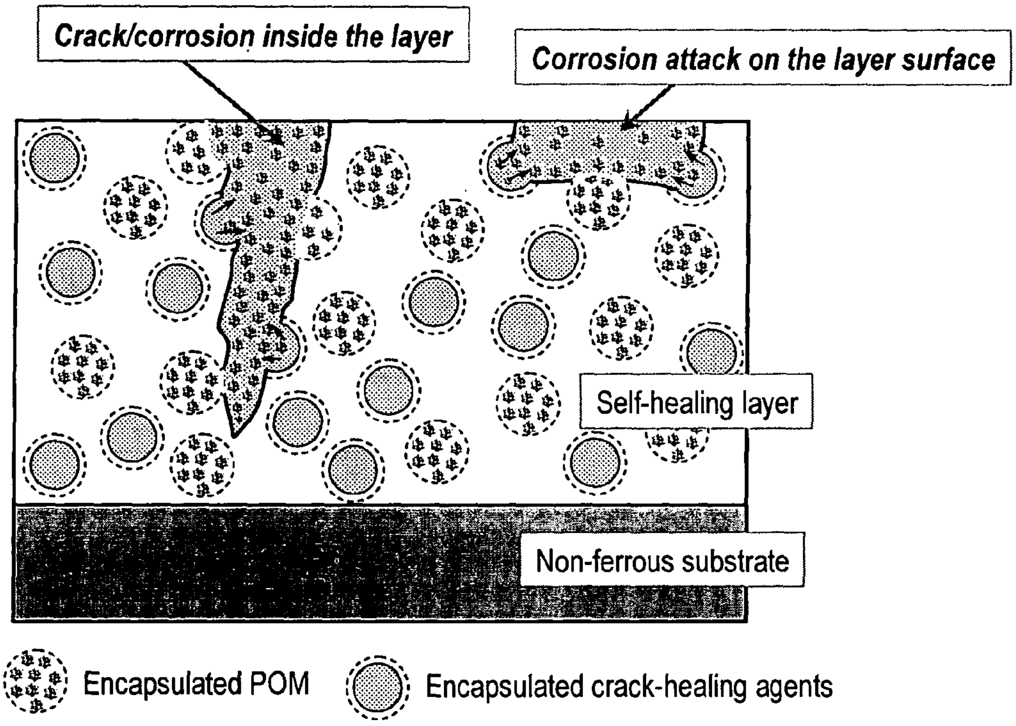
Crack/corrosion inside the layer
Corrosion attack on the layer surface
Self-healing layer
Non-ferrous substrate
Encapsulated POM
Encapsulated crack-healing agents

Figure 2.

**European Patent Office**

## EUROPEAN SEARCH REPORT

Application Number
EP 06 07 5365

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| | | | C23C<br>C25D<br>C23F |

The present search report has been drawn up for all claims

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| Munich | 18 May 2006 | Ramos Flores, C |

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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# ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 06 07 5365

18-05-2006

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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