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(54) Title: METHOD FOR THE POST-TREATMENT OF METAL LAYERS

(57) Abstract: This invention relates to a method for the post-treatment of metal layers, especially for the post-treatment of metal layers deposited on the surface of a substrate. With the invention a method for the post-treatment of a metal surface is proposed, wherein the metal surface is brought into contact with a corrosion resistance increasing solution, characterised in that during the contacting of the metal surface with the corrosion resistance increasing solution a current is applied between the surface and a counter electrode, whereby the surface is anodic contacted and the counter electrode is cathodic contacted.



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METHOD FOR THE POST-TREATMENT OF METAL LAYERS

[0001] This application claims priority to European application 09002335.9 filed February 19, 2009 and European application 08019899.7 filed November 14, 2008, the entire disclosures of which are incorporated by reference.

[0002] This invention relates to a method for the post-treatment of metal layers, especially for the post-treatment of metal layers deposited on the surface of a substrate.

[0003] It is well-known in the art of surface technology to post-treat metal layers deposited on a substrate surface, either by galvanic deposition, autocatalytic deposition or other methods like PVD or CVD, to adjust the surface characteristics or features. One of the main features intended to increase is the corrosion resistance of the surface layer.

[0004] For example, European patent application EP 1 712 390 discloses the coating of metal surfaces with corrosion inhibiting polymer layers. Here, the surface is contacted with a solution comprising a polyvinyl phosphonic acid or polyacrylic acid prior to a treatment of the surface with a solution comprising monomeric or polymeric resins or a mixture of monomeric and polymeric resins.

[0005] US 6,030,710 discloses aluminium alloy sheets which are provided with the primer layer comprising a reaction product of aluminium oxide or hydroxide and a polyvinyl phosphonic acid/polyacrylic acid copolymer, which primer layer is coated with the polymer coating composition containing polyvinyl chloride or an epoxy.

[0006] US 6,696,106 B1 discloses a primer for radiation cureable coating compositions. Here, an aluminium-polymer composite is made by coating a surface portion of an aluminium alloy body with the primer composition comprising a polyvinyl phosphonic acid/polyacrylic acid copolymer to form a primer layer, coating the primer layer with the radiation cureable polymer precursor, and irradiating the polymer precursor with ultraviolet or electron beam radiation.

[0007] US 6,020,030 also discloses the pre-treatment of aluminium alloy substrates with an aqueous solution containing an organophosphorous compound, preferably a polyvinyl phosphonic acid/polyacrylic acid copolymer, before coating the substrate with the polymer.

[0008] WO 2004/074372 A1 discloses a composition for treating surfaces, said composition containing copolymer as component A comprising in (meth) acrylic acid or the

salts thereof, a monomer containing carboxylate and/or monomers comprising groups containing phosphoric acid and/or phosphonic acid or the salts thereof and optionally additional comonomeres. Furthermore, a passivation layer is disclosed, which contains the component A and is applied to a metallic surface.

[0009] While the methods known from the state of the art to post-treat metal layers are more or less capable to increase the corrosion resistance of the metal layers, some of the environmental or application depending influences are so aggressive that layers, also when treated according to the state of the art, cannot restrain from corrosion.

[0010] Amongst others, the chloride induced corrosion of chromium surfaces caused by deicing salts has been a major topic for several years in the field of automotive. Also, the so called red-rust on chromium surfaces that have been plated with trivalent chromium electrolytes is a problem known from the state of the art.

[0011] In another field of application, the fitting industry, Pb-leaching of brass parts for drinking water pipe applications is known to be a problem. The Pb-leaching should be minimised by passivation of the brass metal.

[0012] In the art of decorative coatings, there are intentions to reduce the sensitivity of the surface against fingerprints. To do so, it is known from the state of the art to incorporate polymeric components into a metal layer deposited on the surface, like for example polytetrafluoroethylene particles.

[0013] A drawback of the methods known from the state of the art is that the surfaces still showing some corrosive reactions or that the post-treatment layers increasing the corrosion resistance are not adhered enough to the surface to enable long term corrosion resistance.

[0014] It is therefore the object of this invention to provide a method which is capable to enhance the corrosion resistance of metal layers deposited on the surface of substrates.

[0015] To do so, the invention proposes a method for the post-treatment of a metal layer deposited on the surface of a substrate, wherein the metal layer after deposition is brought into contact with a corrosion resistant increasing solution, which method is characterised in that during the contacting of the metal layer with the corrosion resistance increasing solution a current is applied between the surface of the metal layer and a counter electrode, whereby the metal layer is anodic contacted and the counter electrode is cathodic contacted.

[0016] This kind of post-treatment is capable to increase the corrosion resistance of metal layers like, for example nickel layers, copper layers, chrome layers, zinc layers, tin layers, silver layers, iron layers, manganese layers, molybdenum layers, gold layers, platinum layers, ruthenium layers, palladium layers, rhodium layers and lead layers or layers of alloys comprising at least one of the before mentioned metals, like for example Ni-P-alloy layers, brass layers, bronze layers, nickel-silver layers, coin-metal layers, or type-metal layers.

[0017] While being mainly directed to metal layers deposited on an substrate surface, the inventive method is also capable to increase the corrosion resistance of metal surfaces in general, like for example the surfaces of substrates made of steel or stainless steel, brass, or bronze.

[0018] The solution to be used within the inventive method can be an aqueous corrosion resistance increasing solution, which means an aqueous solution comprising a compound which is capable to increase the corrosion resistance of the metal layer deposited.

[0019] Examples for such compounds increasing the corrosion resistance of layers are, for example compounds having moieties like anions of the group consisting of phosphates, phosphonates, phosphinates, nitrates, borates, silicates, molybdates, tungstates, carboxylates and oxalates.

[0020] In an embodiment of the inventive method, the corrosion resistance increasing solution comprises a compound having hydrophobic carbon-chains with hydrophilic anionic functional groups. Such functional groups may be phosphate-groups, phosphonate-groups, sulphate-groups, sulphonate-groups, or carboxyl-groups. Such compounds having hydrophobic carbon-chains with a hydrophilic anionic functional group are, for example polyvinyl phosphonic acid and/or polyacrylic acid, and/or copolymers of such acids.

[0021] Other examples for a compound having hydrophobic carbon-chains with a hydrophilic anionic functional group are alkylphosphonic acids or alkylsulfonic acids having 10 to 26 carbon atoms.

[0022] According to the inventive method, the current density of the applied current can be in a range between 0,001 A/dm² and 100 A/dm², with a preferred range between 0,02 A/dm² and 10 A/dm². This current can be applied for a time between 0,001 seconds and 10 minutes, preferably between 30 seconds and 3 minutes. When using a low current density within the inventive method, the time the current is applied has to be higher, for example within

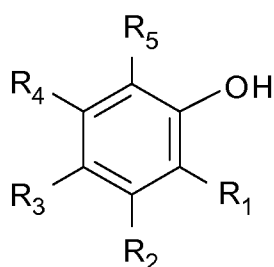
the range of minutes, while high current densities will needed to be applied only for short times, like for example within the range of milliseconds or seconds.

[0023] It is believed that by the appliance of the anodic current, the oxide layer on the metal or metal layer surface is removed, thereby enabling the corrosion resistance increasing compounds to react with the metal. In this the inventive method differs from the anodic treatment known for aluminium surfaces, where by an anodic current an oxide layer on the metal surface is formed.

[0024] Anodic current in the meaning of the invention is as any kind of current having an anodic portion. Therefore, not only pure anodic direct current can be applied, but also alternating current. Also, it is possible to apply the current as a pulse, like it is known from pulse or pulse-revers plating operations.

[0025] Surprisingly, a further improvement of the above described method is found by the addition of an aromatic compound having at least one hydroxy group, like phenole or its derivates. Especially capable is the addition of an aromatic compound having at least one hydroxy group which comprises a further functional group having a positive inductive effect on the hydroxyl group.

[0026] Aromatic compounds capable to further improve the inventive methods are compounds of the general structure



wherein R1 is H or OH; R2 is H, OH, F, Cl, Br, -O-R, R-OH, R-COOH, R-CHO, R-O-R, R-CO-R, -SH, -NO₂, -CN, -COO-R; and R3 to R5 are independently from each other H, C_nH_{2n+1}, OH, F, Cl, Br, -O-R, R-OH, R-COOH, R-CHO, R-O-R, R-CO-R, -SH, -NO₂, -CN, -COO-R, wherein R is an unsubstituted or substituted alkyl-group having 1 to 10 carbon.

[0027] Compounds according to the above mentioned general structure are, for example phenole, 3-ethoxyphenole, 3,5-dimethoxyphenole, 3-nitrophenole, resorcinol, 4-ethylresorcinol, 4-chlorresorcinol, phloroglucine, pyrogallol, gallic acid, catechol,

dihydroxybenzaldehyde, dihydroxytoluene, 3-hydroxyphenylacetic acid, 3-hydroxybenzoic acid, n-octyl gallat, guajacol and 3,5,7-trihydroxyflavone.

[0028] It was found that at least one further functional group in meta-position to the hydroxy group renders a compound according to the above mentioned general structure to be especially useful within the inventive method.

[0029] The addition of the mentioned aromatic compounds to the inventive corrosion resistance increasing solution in the inventive method surprisingly enables to reduce the concentration of the compound having hydrophobic carbon-chains with hydrophilic anionic functional groups, like polyvinyl phosphonic acid and/or polyacrylic acid, even if the aromatic compound is added only in very small amounts.

[0030] The aromatic compound can be added to the inventive corrosion resistance increasing solution in the inventive method at a concentration between 0,45 mmol and 45 mmol, with a preferred range of 2 mmol to 9 mmol.

[0031] Also when added in such a low concentration, the amount of the compound having hydrophobic carbon-chains with hydrophilic anionic functional groups can be reduced by a coefficient of at least 4 to 5. For example, instead of using 4 g/l of a polyvinyl phosphonic acid/polyacrylic acid copolymer (30/70) in absence of an aromatic compound having a hydroxy group, by addition of such an aromatic compound the concentration of the copolymer can be reduced to 1 g/l only. That gains into a reduction of the costs for the commodities used per square meter by at least four times.

[0032] While not being bound to the theory, the applicant believes that due to the anodic contacting of the metal layer, the metal layer is partly dissolved, thereby forming areas of the metal layer surface which are capable to form covalent bondings between the metal surface and the compounds used for the increase of the corrosion resistance. These effects in a very strong bonding of the compounds and/or anions on the metal surface which gains into a corrosion resistance increasing coating strongly adhered to the metal layer surface. Furthermore, due to the current applied the anions and compounds are forced to react or at least interact with the metal layer surface.

[0033] While not being bound to this theory with respect to the additionally used aromatic compounds having at least one hydroxy group, the applicant believes that the aromatic compound is bound to the metal surface by the hydroxy group in a covalent manner. One

attempt to explain the reaction is that the hydroxy group, during the anodic treatment, is deprotonated offering a free valence at the oxygen of the hydroxy group. This theory can also explain the improvements gained by the use of an aromatic compound comprising in meta-position to the hydroxy group a group having a positive inductive effect. The positive inductive effect supports the deprotonation of the hydroxy group, thereby enabling the reaction pass to form a covalent binding to the metal surface.

[0034] Concerning the use of the inventive method to increase the corrosion resistance of a precious-metal layer, it is known in the art that corrosion of precious-metal layers is not a corrive attack on the precious-metal, but on the metal forming the layer underneath the precious-metal layer. In general, such precious-metal layers show pores and cracks leaving open areas of the metal the precious-metal layer is deposited on, ilke for example nickel or copper. Attempts of the state of the art to increase the corrosion resistance of such layers in general are accompanied with an increase of the thickness of the precious-metal layer to reduce the number of pores and cracks. This boost the amount of precious metal needed per area, thereby directly increasing the cost significantly. It is believed that when performing the inventive method to a precious-metal layer the corrosion resistance increasing compound does not bound to the precious-metal, but to the metal forming the layer underneath the precious-metal layer. Accordingly, there is no need in the inventive method to increase the thickness of the precious-metal layer to achieve a surface having excellent corrosion resistance. This allows to use very thin precious-metal platings only and to reduce the costs per area in a significant manner.

[0035] A further field of application for the inventive method as well as the inventive corrosion resistance increasing solution is to prepare a metal layer for varnishing it. To varnish a metal layer by lacquer or varnish becomes more and more important in the art of surface finishing. One problem occurring when varnishing metal surfaces is the weak adhesion of the varnish or lacquer to the metal surface. Here, the inventive method and the inventive solution can be used to form a primer on the metal surface. The primer increases the adhesion of the varnish to the metal surface.

[0036] Advantageously, in the inventive method the primer can be adapted to the varnish or lacquer used. Such an adaption can be especially performed by variation of the aromatic compound having a hydroxy group comprised in the inventive post-treatment solution.

[0037] An example for such a use of the inventive method in the art of vanishing is to varnish chrome-wheels in the automotive industry. Here, for example after deposition of a

chromium layer on the wheel a mask is put on the chromium surface to transfer a specific pattern to the surface by a lacquer. By appliance of the inventive method to the wheel prior to the varnishing the adhesion of the lacquer to the chromium surface is improved in a significant manner, and at the same time the corrosion resistance of the chromium layer is increased.

[0038] The invention is explained in terms of examples in the following, while not being limited to these examples only.

Example 1:

[0039] A microporous chromium plated grill is brought into contact in a post-treatment procedure with an aqueous solution comprising 30 g/l of a polyvinyl phosphonic acid/polyacrylic acid copolymer at a temperature of 60°C. An anodic current of 0,05 A/dm² is applied between the microporous chromium plated grill and a stainless steel counter electrode for 2 minutes. The resulting layer shows a strong improvement of the corrosion resistance against CaCl₂ containing corrosion media in the so called "Russian Mud Test". The grill was covered with a mixture containing 10 ml water, 2 g CaCl₂, and 10 g Kaolin. After 168 h testing at 50°C the surface of the chromium plated grill showed no visible corrosion attack.

Example 2:

[0040] A microcracked chromium plated grill is brought into contact in a post-treatment procedure with an aqueous solution comprising 5 g/l of a polyvinyl phosphonic acid/polyacrylic acid copolymer and 5 g/l sodiumphosphate at a temperature of 60°C. An anodic current of 0,15 A/dm² is applied between the microcracked chromium plated grill and a stainless steel counter electrode for 1 minute. The resulting layer shows a strong improvement of the corrosion resistance against CaCl₂ containing corrosion media in the so called "Russian Mud Test". The resulting layer shows also after a treatment with solvents like acetone the same resistance against such CaCl₂ containing corrosion media as before.

Example 3:

[0041] A hard chromium plated valve is brought into contact in a post-treatment procedure with an aqueous solution comprising 5 g/l of a polyvinyl phosphonic acid/polyacrylic acid copolymer and 5 g/l sodium metasilicate at a temperature of 80°C. An anodic current of 0,25 A/dm² is applied between the hard chromium plated valve and a stainless steel counter

electrode for 1 minute. The resulting layer shows a strong improvement of the corrosion resistance in the copper accelerated salt spray test (CASS).

Example 4:

[0042] A hard chromium plated valve is brought into contact in a post-treatment procedure with an aqueous solution comprising 6 g/l of a polyvinyl phosphonic acid and 5 g/l sodium metasilicate at a temperature of 80°C. An anodic current of 0,25 A/dm² is applied between the hard chromium plated valve and a stainless steel counter electrode for 1 minute. The resulting layer shows a strong improvement of the corrosion resistance in the copper accelerated salt spray test (CASS).

Example 5:

[0043] A hard chromium plated valve is brought into contact in a post-treatment procedure with an aqueous solution comprising 7 g/l of a polyacrylic acid copolymer and 5 g/l sodium metasilicate at a temperature of 80°C. An anodic current of 0,25 A/dm² is applied between the hard chromium plated valve and a stainless steel counter electrode for 1 minute. The resulting layer shows a strong improvement of the corrosion resistance in the copper accelerated salt spray test (CASS).

Example 6:

[0044] A steel panel first was plated with a bright nickel layer. On the nickel layer a chromium layer was deposited from a trivalent chromium electrolyte. The so plated steel panel was brought partly into contact in a post-treatment procedure with an aqueous solution comprising 2,5 g/l of an alkylphosphonic acid (C₁₈), 25 g/l butylglycole, 10 g/l phosphonic acid, and 0,2 g/l ethylhexylsulphate at a temperature of 60°C. An anodic current of 0,05 A/dm² is applied between the panel and a stainless steel counter electrode for 30 seconds. The resulting layer shows a strong improvement of the corrosion resistance in neutral salt spray test (NSS). The untreated area of the partly post-treated panel shows after 24 h red rust (pin hole corrosion). The post-treated area shows first red rust after 72 h NSS.

Example 7:

[0045] A chromium plated bath room fitting with a dull pearlbright finish is brought into contact in a post-treatment procedure with an aqueous solution comprising 10 g/l of a polyvinyl phosphonic acid/polyacrylic acid copolymer at a temperature of 60°C. An anodic

current of 0,05 A/dm² is applied between the chromium plated bathroom fitting and a stainless steel counter electrode for 2 minutes. The resulting layer shows a surface, which is less sensitive against fingerprints in comparison to non-post-treated pearl-brite surfaces.

Example 8:

[0046] A nickel and chromium plated bathroom fitting with brass as substrate was brought partly into contact in a post-treatment procedure with an aqueous solution comprising 0,5 g/l of an alkylphosphonic acid (C₁₄), 20 g/l butylglycole, 5 g/l benzotriazole, and 0,2 g/l ethylhexylsulphate at a temperature of 50°C. An anodic current of 0,05 A/dm² is applied between the bathroom fitting and a stainless steel counter electrode for 4 minutes. The post-treated bathroom fitting was brought into contact with artificial sweat and stored in this for 168 h. After this the Ni, Cu and Pb concentration in the artificial sweat solution, that was leached out from the bathroom fitting was 90% less than for an untreated bathroom fitting under same test conditions.

Example 9:

[0047] A microporous chromium plated grill is brought into contact in a post-treatment procedure with an aqueous solution comprising 4 g/l of a polyvinyl phosphonic acid/polyacrylic acid copolymer (30/70) and 5 g/l sodium orthophosphite at a temperature of 60°C and a pH of 3.5. An anodic current of 0,2 A/dm² is applied between the microporous chromium plated grill and a stainless steel counter electrode for 2 minutes. The resulting layer shows a strong improvement of the corrosion resistance against CaCl₂ containing corrosive media in the so called "Nissan-Test. For the Nissan test a mixture of kaolin, CaCl₂, and water is applied to the metal surface of the chromium plated grill which is stored at a temperature of 60°C for 48h to 168h. After storage the visible corrosion attack caused by the applied CaCl₂-containing media is used to classify the corrosion resistance of the tested metal surface.

Example 10:

[0048] A microporous chromium plated grill was post-treated like explained in example 7, with the difference that the aqueous solution comprises 1 g/l of a polyvinyl phosphonic acid/polyacrylic acid copolymer (30/70) only, 0,5 g/l resorcinol, and 5 g/l sodium-orthophosphite. The resulting layer had the same corrosion resistance like the layer in example 7.

Example 11:

[0049] A nickel plated article for jewellery application is plated last with a bright silver layer. The so plated article is brought partly into contact in a post-treatment procedure with an aqueous solution comprising 5g/l of polyacrylic acid, 10g/l sodiumphosphonate, 6 g/l phosphoric acid and 1 g/l guajacol at a temperature of 60°C. An anodic current of 0,01 A/dm² is applied between the article and a stainless steel counter electrode for 5 minutes. The resulting layer shows a strong decrease of discolouration after storing it for 3 minutes in an aqueous solution comprising 3% of ammoniumsulfide.

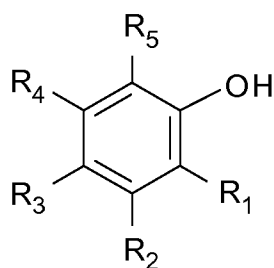
Example 12:

[0050] A chromium plated wheel rim is brought into contact in a post-treatment procedure with an aqueous solution comprising 2g/l sodiumphosphite and 15 g/l of a polyvinyl phosphonic acid at 50°C. An anodic current of 1 A/dm² is applied between the chromium plated wheel rim and a stainless steel counter electrode for 15 seconds. After this time the resulting layer shows strong hydrophilic properties. Therefore a water-based lacquer or even a two-component-acrylic lacquer is easy to apply on the post-treated chromium surface and the final varnishing system shows a strong improvement of adhesion to the chromium surface.

WHAT IS CLAIMED:

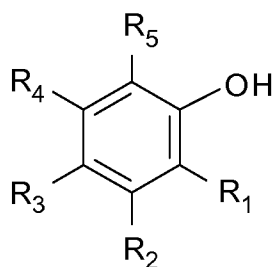
1. Method for the post-treatment of a metal surface, wherein the metal surface is brought into contact with a corrosion resistance increasing solution, characterised in that during the contacting of the metal surface with the corrosion resistance increasing solution a current is applied between the surface and a counter electrode, whereby the surface is anodic contacted and the counter electrode is cathodic contacted.
2. Method according to claim 1, wherein the metal surface is a metal of the group consisting of nickel, copper, chrome, zinc, tin, silver, iron, manganese, molybdenum, gold, platinum, ruthenium, palladium, rhodium, and lead or an alloy comprising at least one of these metals.
3. Method according to one of the preceding claims, wherein the current density of the applied current is set to a range in between 0,001 A/dm² and 100A/dm², preferably between 0,02 A/dm² and 10 A/dm².
4. Method according to one of the preceding claims, wherein the current is applied for a time between 0,001 seconds and 10 minutes, preferably between 1 second and 5 minutes, more preferred between 30 seconds and 3 minutes.
5. Method according to one of the preceding claims, wherein the metal surface is brought into contact with an aqueous corrosion resistance increasing solution.
6. Method according to one of the preceding claims, wherein the metal surface is brought into contact with a corrosion resistance increasing solution comprising anions of the group consisting of phosphates, phosphonates, phosphinates, nitrates, borates, silicates, molybdates, tungstates, carboxylates and oxalates.
7. Method according to one of the preceding claims, wherein the substrates surface is brought into contact with the corrosion resistance increasing solution comprising a compound having hydrophobic carbon-chains with a hydrophilic anionic functional group.
8. Method according to claim 7, wherein the hydrophilic anionic functional group of the hydrophobic carbon-chain is at least one of a phosphate-group, a phosphonate-group, a sulphate-group, a sulphonate-group, or a carboxyl-group.
9. Method according to one of the preceding claims, wherein the metal surface is brought into contact with a corrosion resistance increasing solution comprising a polyvinyl phosphonic acid and/or an polyacrylic acid, and/or copolymers of such acids.

10. Method according to one of the preceding claims, wherein the corrosion resistance increasing solution further comprises an aromatic compound having at least one hydroxy-group.
11. The method according to claim 10, wherein the aromatic compound comprises in meta-position to the hydroxy-group a group having a positive inductive effect.
12. Method according to claim 10 or 11, wherein the aromatic compound is of the general structure



wherein R1 is H or OH; R2 is H, OH, F, Cl, Br, -O-R, R-OH, R-COOH, R-CHO, R-O-R, R-CO-R, -SH, -NO₂, -CN, -COO-R; and R3 to R5 are independently from each other H, C_nH_{2n+1}, OH, F, Cl, Br, -O-R, R-OH, R-COOH, R-CHO, R-O-R, R-CO-R, -SH, -NO₂, -CN, -COO-R, wherein R is an unsubstituted or substituted alkyl-group having 1 to 10 carbon atoms.

13. Method according to one of the claims 10 to 12 wherein the aromatic compound is at least one of phenole, 3-ethoxyphenole, 3,5-dimethoxyphenole, 3-nitrophenole, resorcinol, 4-ethylresorcinol, 4-chlorresorcinol, phloroglucine, pyrogallol, gallic acid, catechol, dihydroxybenzaldehyde, dihydroxytoluene, 3-hydroxyphenylacetic acid, 3-hydroxybezoic acid, n-octyl gallat, guajacol, and 3,5,7-trihydroxyflavone.
14. Method according to one of the preceding claims, wherein the metal surface subsequent to conducting the method is varnished.
15. Solution for the anodic post-treatment of metal surfaces comprising anions of the group consisting of phosphates, phosphonates, phosphinates, nitrates, borates, silicates, molybdates, tungstates, carboxylates, and oxalates; an acid of the group consisting of polyvinyl phosphonic acid, polyacrylic acid, alkylphosphonic acid, and alkylsulfonic acid, or mixtures or copolymers of such acids; and an aromatic compound having a hydroxy-group of the general structure



wherein R₁ is H or OH; R₂ is H, OH, F, Cl, Br, -O-R, R-OH, R-COOH, R-CHO, R-O-R, R-CO-R, -SH, -NO₂, -CN, -COO-R; and R₃ to R₅ are independently from each other H, C_nH_{2n+1}, OH, F, Cl, Br, -O-R, R-OH, R-COOH, R-CHO, R-O-R, R-CO-R, -SH, -NO₂, -CN, -COO-R, wherein R is an unsubstituted or substituted alkyl-group having 1 to 10 carbon atoms.

16. Solution according to claim 15, wherein the aromatic compound having a hydroxy-group is at least one of phenole, 3-ethoxyphenole, 3,5-dimethoxyphenol, 3-nitrophenole, resorcinol, 4-ethylresorcinol, 4-chlorresorcinol, phloroglucine, pyrogallol, gallic acid, catechol, dihydroxybenzaldehyde, dihydroxytoluene, 3-hydroxyphenylacetic acid, 3-hydroxybezoic acid, n-octyl gallat, guajacol, and 3,5,7-trihydroxyflavone.
17. Use of a solution according to one of the claims 15 or 16 as primer for a metal surface for a subsequent varnishing of the surface.

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2009/038348

A. CLASSIFICATION OF SUBJECT MATTER

INV. C25D9/04 C09D5/44 C09D5/08 C23F13/00

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)

C25D C09D C23F

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 practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 10 2005 020767 A1 (ECKART GMBH & CO KG [DE]) 9 November 2006 (2006-11-09) paragraphs [0007], [0011], [0017], [0018], [0020], [0026] - [0028], [0041], [0076] - [0080], [0089], [0130] claims 1-22	1, 2, 4-9
X	GB 1 135 406 A (FORD MOTOR CO) 4 December 1968 (1968-12-04) page 1 claims 1-30 page 2, line 100 - page 3, line 40 page 4, line 109 - page 5, line 25 ----- -/--	1, 2, 4-9

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"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

15 September 2009

Date of mailing of the international search report

23/09/2009

Name and mailing address of the ISA/

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Authorized officer

Haering, Christian

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2009/038348

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 16 21 882 B1 (FORD WERKE AG) 30 December 1971 (1971-12-30) column 1, lines 1-41 column 3, lines 11-41 column 4, line 69 - column 5, line 13 examples 10-12	1-9
X	RAMMELT U ET AL: "Improvement of protection performance of polypyrrole by dopant anions" JOURNAL OF APPLIED ELECTROCHEMISTRY, KLUWER ACADEMIC PUBLISHERS, DO, vol. 35, no. 12, 1 December 2005 (2005-12-01), pages 1225-1230, XP019247338 ISSN: 1572-8838 abstract	1-6,10
X	US 2 377 792 A (LAWRENCE CHARLES K ET AL) 5 June 1945 (1945-06-05) page 1, left-hand column, line 50 - page 1, right-hand column, line 9 page 3, left-hand column, line 32 - page 4, left-hand column, line 2 claims 1,2	1,2,5,6
X	FR 1 592 078 A (BERNARD LE BOUCHER) 11 May 1970 (1970-05-11) page 1 examples 1-9	1-6
X	WO 2004/074372 A (BASF AG [US]; DIETSCHE FRANK [DE]; WITTELER HELMUT [DE]; KLUEGLEIN MAT) 2 September 2004 (2004-09-02) abstract pages 1-6 pages 15-18 claims 1-3,6-9	1-17
X	EP 1 288 334 A (NIPPON STEEL CORP [JP]; MITSUBISHI MOTORS CORP [JP]) 5 March 2003 (2003-03-05) abstract paragraphs [0022] - [0030] paragraphs [0036], [0037] claims 1,2	1,2,5-7
X	US 3 350 285 A (SUSUMU NISHIGAKI ET AL) 31 October 1967 (1967-10-31) abstract column 2, lines 51-60 claims 1-5	1-5,7,8

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2009/038348

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This International search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers allsearchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.2

Claims Nos.: -

The initial phase of the search revealed a very large number of documents relevant to the issue of novelty. So many documents were retrieved that it is impossible to determine which parts of the claims may be said to define subject-matter for which protection might legitimately be sought (Articles 6 and 5 PCT). For these reasons, a meaningful search of the whole claimed subject matter of claims 1 to 5 could not be carried out completely. The extent of the search was consequently limited (PCT Guidelines 9.19 and 9.23).

Furthermore, the subject-matter of claim 1 extend beyond the scope of the invention leading to a lack of unity. Indeed, most of the examples (1-5, 7,9-12) are referring to a polymer coating, particularly a polyvinyl phosphonic acid/polyacrylic acid copolymer (examples 1-3,7,9,10), whereas examples 6 and 8 refer to a post treatment with a phosphonic acid and butylglycol. This cannot be considered as similar post treatments according to Article 6 PCT.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guideline C-VI, 8.2), should the problems which led to the Article 17(2)PCT declaration be overcome.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2009/038348

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