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

(11) **EP 1 550 740 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
09.03.2011 Bulletin 2011/10

(51) Int Cl.:
C23C 22/73 *(2006.01)* ***C23C 22/80*** *(2006.01)*
C23C 22/36 *(2006.01)*

(21) Application number: **04028997.7**

(22) Date of filing: **07.12.2004**

(54) **Multiple step conversion coating process**

Mehrstufenverfahren zur Konversionsbeschichtung

Procédé de couche de conversion à plusieurs étapes

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

(30) Priority: **29.12.2003 US 745539**

(43) Date of publication of application:
06.07.2005 Bulletin 2005/27

(73) Proprietor: **Henkel AG & Co. KGaA**
40589 Düsseldorf (DE)

(72) Inventors:
- **Schenzle, Bernd**
  69123 Heidelberg (DE)
- **Sienkowski, Michael L.**
  48093 Warren,
  Michigan (US)
- **Goodreau, Bruce H.**
  Romeo, MI 48065 (US)

(56) References cited:

EP-A- 0 434 358	**EP-A- 0 653 502**
EP-A- 0 801 149	**EP-A- 1 225 250**
EP-A- 1 371 756	**WO-A-01/32953**
WO-A-99/12661	**WO-A-02/066702**
DE-A1- 10 118 552	**DE-A1- 19 705 701**
FR-A- 2 389 683	**GB-A- 1 498 718**
GB-A- 2 136 454	**US-A- 5 024 707**
US-A- 5 584 946	**US-B1- 6 368 426**

EP 1 550 740 B1

Description

A. Field of the Invention

[0001] The present invention relates to a multiple step, low temperature, low sludge-producing, low phosphate, corrosion-prevention pretreatment process suitable for simultaneous processing of steel, zinc, and aluminum substrates.

B. Description of the Related Art

[0002] For many reasons, such as weight, rigidity or recyclability, aluminum is increasingly used in vehicle construction. As used herein, the expression "aluminum" refers not only to pure aluminum but also to aluminum alloys whose main component is aluminum. Examples of commonly used alloying elements are silicon, magnesium, copper, manganese, chromium and nickel. The total proportion by weight of these alloying elements in the alloy normally do not exceed 10%. Whereas engine and gear parts, wheels, seat frames, etc. already contain large amounts of aluminum, the use of aluminum in bodywork construction is presently still restricted to parts such as hoods, rear trunk lids, inner door parts and various small parts as well as truck cabins, side walls of transporters or attachments to minivans. Overall, worldwide less than 5% of the metal surface of automobile bodies is made of aluminum. The increased use of aluminum in this sector is being intensively investigated by the aluminum and automobile industries.

[0003] Today many automobile parts are made from a variety of materials, including but not limited to aluminum, magnesium, steel, and zinc. Preferably, such prefabricated metal components are provided with a phosphate coating. The aim of phosphating metals is to produce firmly adhering metal phosphate layers on the metal surface that improve the corrosion resistance, and, in conjunction with paints or other organic coatings, contribute to a substantial improvement of the coating adhesion and resistance to creepage under corrosive stress.

[0004] Such phosphating processes have been known for a long time. For the pretreatment before painting, especially before electro-dipcoating, low zinc phosphating processes are used. It is well known that zinc phosphate conversion coatings, particularly those of the "low zinc" type, are capable of producing excellent corrosion-protective undercoatings for subsequent painting. It has been generally regarded in the prior art that two important characteristics of a "low zinc" phosphating liquid composition are a phosphate concentration of at least 5 grams per liter of composition, this unit of concentration being hereinafter usually abbreviated as "g/l", more preferably at least 10 g/l, and a weight ratio of phosphate-to-zinc concentrations that is at least 10:1. A basic parameter in these low zinc phosphating baths is the weight ratio of phosphate ions to zinc ions, which is normally above 8 and may reach values of up to 30.

[0005] Generally only one phosphating installation is available in an automobile factory. Therefore, it is necessary to be able to carry out phosphating operations at such factories in a mixed operation on automobile components made entirely of steel, entirely of aluminum, entirely of zinc, or a combination of steel, aluminum, and zinc in varying proportions.

[0006] However, in practice it has been found that in the joint phosphating of surfaces of aluminum, zinc, steel and/or galvanized steel substrates, technical compromises have to be made regarding the composition of the phosphating baths. Aluminum ions released from the aluminum surface by the etching and pickling action act as a bath poison for the phosphating solution and interfere in the formation of zinc phosphate crystals on iron (steel) surfaces. The dissolved aluminum must therefore be precipitated or masked by appropriate measures. For this purpose free or complex-bound fluoride ions are normally added to the phosphating baths.

[0007] The fluoride ions mask the aluminum ions by complex formation and/or precipitate these ions as hexafluoroaluminates of sodium and/or potassium if the solubility products of the corresponding salts are exceeded. Furthermore, free fluoride ions usually lead to an increased etching attack on the aluminum surfaces, with the result that a more or less closed and sealed zinc phosphate layer can form on the latter.

[0008] The joint phosphating of aluminum structural portions with those of zinc, steel and/or galvanized steel thus has the technical disadvantage that the phosphating baths have to be very accurately monitored as regards their fluoride content. This increases the control and monitoring work involved and may require stocking and metering of fluoride-containing solutions as separate replenishment solutions. Also, the precipitated hexafluoroaluminate salts increase the amount of phosphating sludge and raise the cost of its removal and disposal.

[0009] It is well known that zinc phosphate conversion coating processes produce a solid byproduct called "sludge" in addition to the desired solid conversion coating on the metal being phosphated. In order to continue using a liquid conversion coating composition, sludge eventually has to be removed from the bath and disposed of in an approved landfill site. Sludge reduction is desirable because the number of available landfill sites for disposal of this byproduct is dwindling and known recycling alternatives through chemical treatment are not economical at this time.

[0010] A typical zinc phosphating bath includes phosphate ions, divalent metal ions, hydrogen ions, and an oxidizing compound such as nitrite or chlorate as the process accelerator. The mechanism of the reaction involves acid attack on the substrate metal, iron (steel or zinc) in this instance, at micro anodes and deposition of phosphate crystals at micro cathodes. It also involves the liberation of hydrogen and the formation of phosphate sludge. Changes in the accelerator

can affect the amount of sludge formed. For example, the lower the amount of nitrite accelerator, the greater the amount of sludge formed during the process. U.S. Patent No. 5,900,073**,** discloses how varying the process conditions of a phosphate bath effects the amount of sludge produced by the bath.

[0011] It is also desirable to provide high-quality, phosphate coatings at a lower operating temperature than has been generally used heretofore to obtain highly corrosion-resistant undercoats for paint. Such lower temperatures would reduce the energy costs associated with production of such coatings.

[0012] Simultaneous phosphating of composite metal structures that contain aluminum and/or aluminum alloy in addition to steel and/or galvanized steel portions has been proposed in the art. For example, the in International Patent Application No. WO 99/12661 proposes such a process for simultaneous phosphating of composite structures made of steel and aluminum. Despite rectifying the need to make technical compromises in the simultaneous phosphating process, WO 99/12661 requires pretreating such composite structures with a zinc phosphate bath containing high levels (5 to 40 g/l) of phosphate and low levels (0.01 to 0.2 g/l) of nitrite accelerator, and at a high temperature of 20 °C to about 65 °C.

[0013] German Patent Application No. DE 197 35 314 also sets forth a process for simultaneous phosphating of composite structures. Like WO 99/12661**,** however, DE 197 35 314 requires pretreating such composite structures with a zinc phosphate bath containing high levels (14 g/l) of phosphate, and at an even higher temperature of 40°C to 70°C. DE 197 35 314 fails to discuss use of a nitrite as an accelerator.

[0014] Thus, both processes set forth in WO 99/12661 and DE 197 35 314 create excessive amounts of undesirable sludge due to the high phosphate and/or low nitrite content of the phosphate bath, and operate at undesirably high temperatures which increases the energy costs of the process.

[0015] Accordingly there exists a need for pretreatment processes for composite structural parts or substrates, for example automobile bodies that contain besides aluminum portions, zinc portions, and/or steel and/or galvanized steel portions, that reduces the sludge produced by the process, the temperature at which the process operates, and the need for monitoring the process. The result of the overall pretreatment should be the formation of a conversion layer on all exposed metal surfaces that is suitable as a corrosion-preventing paint substrate, especially before a cathodic electro-dipcoating.

SUMMARY OF THE INVENTION

[0016] The present invention solves the needs of the related art by providing a process for the chemical pretreatment, before an organic coating, of composite metal structures that contain aluminum or aluminum alloy portions together with zinc or zinc alloy portions, and steel, galvanized steel and/or alloy-galvanized steel portions, such that the phosphate level and the operating temperature of the zinc phosphate bath is reduced, and the nitrite accelerator level of the bath is increased. The process of the present invention reduces the sludge produced by the process, the temperature at which the process operates, and the need for monitoring the process. Furthermore, the pretreatment process of the present invention forms a conversion layer on all exposed metal surfaces that is suitable as a corrosion-preventing paint substrate, especially before a cathodic electro-dipcoating.

[0017] In accordance with the purpose of the invention, as embodied and broadly described herein, the invention comprises a process for chemical pretreatment, before an organic coating, of a composite metal structure that contains at least one aluminum or aluminum alloy portion, at least one zinc or zinc alloy portion, and at least one steel, galvanized steel or alloy-galvanized steel portion, the process comprising: (I) treating the composite metal structure with a zinc phosphating solution having less than 5 g/l of phosphate ions and more than 0.2 g/l of nitrite ions, the zinc phosphating solution forming a surface-covering crystalline zinc phosphate layer having a coating weight in the range from 0.5 to 5 grams per meter squared (hereinafter abbreviated as g/m^2) on the zinc or zinc alloy portions, and the steel, and galvanized and/or alloy-galvanized steel portions, but without forming a zinc phosphate layer on the aluminum or aluminum alloy portions; and (II) subsequently, with or without intermediate rinsing with water, contacting the composite metal structure with a treatment solution with a pH in the range from 3.3 to 10 that does not dissolve more than 60% of the crystalline zinc phosphate layer formed on the zinc or zinc alloy portions, and the steel, galvanized and/or alloy-galvanized steel portions, but does produce a conversion layer on the aluminum or aluminum alloy portions wherein the zinc phosphating solution used in step (I) further comprises: a) 0.30 to 3.0 g/l of zinc cations; b) 0.05 to 2.0 g/l of manganese (II) cations; wherein the zinc phosphating solution in step (I) has a free acid value of -1.0 to 3.0 points and a concentration of free fluoride ions in the zinc phosphating solution according to process step (I), measured in g/l, at a specific temperature T (in °C) that is below a value of 8/T.

[0018] The stipulation that no zinc phosphate layer is to be formed on the aluminum portions in the treatment step (I) is to be understood to mean that no closed and sealed crystalline layer is formed and that the mass per unit area of any deposited zinc phosphate does not exceed 0.5 g/m^2. In order to satisfy this condition, the phosphating baths may be arbitrarily formulated as long as specific conditions for the fluoride concentration are observed. Such fluoride concentration conditions may be found in **European Patent No.** 0 452 638 B1**.** According to this disclosure the concentration of free fluoride ions, measured in g/l, should satisfy the condition that, at a specific temperature T (in °C), it lies above a value

of 8/T. Since, however, within the scope of the present invention no zinc phosphate layer should be formed on aluminum in the phosphating step (I), at a specific temperature T (in °C) the concentration of free fluoride ions (in g/1) in the phosphating solution must be below 8/T.

DETAILED DESCRIPTION OF EMBODIMENTS OF THE INVENTION

[0019] The following detailed description of the invention does not limit the invention. Instead, the scope of the invention is defined by the appended claims and equivalents thereof.

[0020] Except in the claims and the operating examples, or where otherwise expressly indicated to the contrary, all numerical quantities in this description indicating amounts of material or conditions of reaction and/or use are to be understood as modified by the word "about" in describing the broadest scope of the invention. Practice within the numerical limits stated is generally preferred, however. Also, throughout the description and claims, unless expressly stated to the contrary: percent, "parts of", and ratio values are by weight; the term "polymer" includes "oligomer", "copolymer", "terpolymer", and the like; the description of a group or class of materials as suitable or preferred for a given purpose in connection with the invention implies that mixtures of any two or more of the members of the group or class are equally suitable or preferred; description of constituents in chemical terms refers to the constituents at the time of addition to any combination specified in the description, and does not necessarily preclude chemical interactions among the constituents of a mixture once mixed; specification of materials in ionic form implies the presence of sufficient counterions to produce electrical neutrality for the composition as a whole, and any counterions thus implicitly specified preferably are selected from among other constituents explicitly specified in ionic form, to the extent possible; otherwise such counterions may be freely selected, except for avoiding counterions that act adversely to the objects of the invention; and the term "mole" and its variations may be applied to ionic, chemically unstable neutral, or any other chemical species, whether actual or hypothetical, that is specified by the type(s) of atoms present and the number of each type of atom included in the unit defined, as well as to substances with well defined neutral molecules.

[0021] As used herein, the term "aluminum" refers to pure aluminum as well as aluminum alloy, the term "zinc" refers to pure zinc and zinc alloy, and the term "steel" refers to pure steel, galvanized steel, and alloy-galvanized steel.

[0022] The present invention is drawn broadly to a multiple step, low temperature, low sludging, low phosphate, corrosion-prevention pretreatment process for simultaneous processing of substrates containing steel, zinc, and aluminum. Generally, the process is a two-step pretreatment process having conventional intermediate rinsing and cleansing steps. The first pretreatment step produces little or no zinc phosphate coating on the aluminum, while forming complete, uniform zinc phosphate coatings on the steel and zinc. The second pretreatment step imparts corrosion protection for the aluminum, while not reducing, and preferably improving, the corrosion prevention properties of the zinc phosphate coating applied to the zinc and steel. In the second step, the nature and concentration of the solutions should be chosen so that on the one hand a layer is reliably formed on the aluminum surfaces, but on the other hand the crystalline zinc phosphate layers formed on the steel and zinc surfaces are not excessively damaged.

[0023] The process is particularly intended for use in automobile manufacturing. In automobile manufacturing, car bodies or car body parts that contain structural portions of aluminum and/or its alloys in addition to structural portions of zinc and/or its alloys, and steel and/or galvanized steel are subjected to a conversion chemical pretreatment before they are painted. In this connection a cathodic electro-dipcoating is conventionally used at the present time as the first painting stage. The process according to the invention is particularly suitable as a pretreatment for this stage.

A. The First Process Step

[0024] The zinc phosphate solution used in the first pretreatment step preferably has a low phosphate ion (PO_4^{-3}) concentration of less than 5 g/l of phosphate ions, and a high nitrite ion concentration of greater than 0.2 g/l of nitrite ions, and preferably greater than 0.3 g/l of nitrite ions. The low phosphate, high nitrite conditions reduce the amount of sludge produced by the operation of the solution. Furthermore, the zinc phosphate solution preferably operates at low temperatures, preferably between 20°C and 40°C, and more preferably between 30°C and 35°C. The zinc phosphate solution may comprise many components and be formulated in at least three different manners, as long as the low phosphate ion concentration, high nitrite ion concentration, and low temperature conditions are met.

1. First Type of Zinc Phosphate Solution

[0025] In accordance with one aspect of the present invention, the zinc phosphate solution may comprise low phosphate, high nitrite, and low temperature conditions.

[0026] In accordance with WO 01/32953 and the present invention, the first type of zinc phosphate solution preferably consists essentially of, or more preferably consists of, water and the following components:

(A) a component of dissolved phosphate anions that have a concentration in the working composition that is less than 5.0 g/l;
(B) a component of dissolved zinc cations that have a concentration in the working composition that is at least, with increasing preference in the order given, 0.30, 0.40, 0.50, 0.60, 0.70, 0.75, 0.80, 0.85, 0.90, 0.93, 0.95, or 0.97 g/l and independently preferably is not more than, with increasing preference in the order given, 2.0,1.8, 1.6,1.50,1.40,1.3 5,1.30,1.25,1.20,1.15, 1.10,1.05, or 1.00 g/l; and
(C) a component of dissolved manganese(II) cations that have a concentration in the working composition that is at least, with increasing preference in the order given, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35, 0.40, 0.45, or 0.48g/l and independently preferably is not more than, with increasing preference in the order given, 2.0, 1.5, 1.2, 1.0, 0.90, 0.80, 0.75, 0.70, 0.65, 0.60, 0.55, or 0.50 g/l.
Optionally, the first zinc phosphate solution may also include one or more of the following components:
(D) a component of at least one of:

- dissolved nickel(II) cations that have a concentration in the working composition that is at least, with increasing preference in the order given, 0.10, 0.20, 0.30, 0.40, 0.50, or 0.60 g/l and independently preferably is not more than, with increasing preference in the order given, 2.0, 1.5, 1.3, or 1.1 g/l; and
- dissolved copper cations that have a concentration that is at least, with increasing preference in the order given, 0.0001, 0.0003, 0.0005, 0.0007, 0.0009, 0.0011, 0.0013, 0.0015, 0.0017, 0.0019, or 0.0021 g/l and independently preferably is not more than, with increasing preference in the order given, 0.030, 0.025, 0.020, 0.015, b.010, or 0.070 g/l;

(E) a component of dissolved fluorine-containing anions that have a stoichiometric equivalent as fluoride that is at least, with increasing preference in the order given, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35, 0.40, 0.45, 0.50, or 0. 55 g/l and independently preferably is not more than, with increasing preference in the order given, 2.0, 1.5, 1.2, 1.0, 0.90, or 0.80 g/l;
(F) a component of dissolved nitrate ions that have a concentration in the working composition that is at least, with increasing preference in the order given, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, or 3.9 g/l and independently, at least for economy, preferably is not more than, with increasing preference in the order given, 20, 15, 12, 10, or 8.8 g/l; and
(G) a dissolved accelerator component other than nitrite consisting of at least one substance selected from the group consisting of:

- 0.3 to 4 g/l of chlorate ions;
- 0.05 to 2 g/l of m-nitrobenzene sulphonate ions;
- 0.05 to 2 g/l of m-nitrobenzoate ions;
- 0.05 to 2 g/l of p-nitrophenol;
- 0.005 to 0.15 g/l of hydrogen peroxide in free or bound form;
- 0.1 to 10 g/l of hydroxylamine in free or bound form; and
- 0.1 to 10 g/l of reducing sugar.

2. Second Type of Zinc Phosphate Solution

[0027] In accordance with a second aspect of the present invention, the zinc phosphate solution preferably consists essentially of, or more preferably consists of, water and the following components:

(A) a component of dissolved phosphate anions that have a concentration in the working composition that is less than 5.0 g/l;
(B) a component of dissolved zinc cations that have a concentration in the working composition that is at least, with increasing preference in the order given, 0.30, 0.40, 0.50, 0.60, 0.70, 0.80, 0.90, 1.00, 1,10, 1.20, 1.30, 1.35, 1.40, 1.43, or 1.47 g/l and independently preferably is not more than, with increasing preference in the order given, 3.0, 2.5, 2.2, 2.0, 1.95, 1.90, 1.87, or 1.85 g/l; and
(C) a component of dissolved manganese(II) cations that have a concentration in the working composition that is at least, with increasing preference in the order given, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35, or 0.37g/l and independently preferably is not more than, with increasing preference in the order given, 2.0, 1.5, 1.2, 1.0, 0.90, 0.80, 0.75, 0.70, 0.65, 0.60, 0.55, 0.50, 0.45, or 0.41 g/l.

[0028] One or more of the following components may also be present in the second phosphate solution:

(D) a component of dissolved nickel(II) cations that have a concentration in the working composition that is at least,

with increasing preference in the order given, 0.10, 0.20, 0.30, 0.35, 0.38, 0.40, 0.42, 0.44, or 0.46 g/l and independently preferably is not more than, with increasing preference in the order given, 2.0, 1.5, 1.0, 0.8, 0.7, 0.65, 0.6, 0.57, 0.54 or 0.51 g/l;

(E) a component of dissolved fluorine-containing anions that have a stoichiometric equivalent as fluoride that is at least, with increasing preference in the order given, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.85, 0.9, 0.94, 0.96, 0.98, 1.0, 1.02, or 1.04 g/l and independently preferably is not more than, with increasing preference in the order given, 2.0, 1.5, 1.3, 1.2, 1.15, 1.1, or 1.05 g/l;

(F) a component of dissolved nitrate ions that have a concentration in the working composition that is at least, with increasing preference in the order given, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.2, 5.4, 5.6, or 5.8 g/l and independently, at least for economy, preferably is not more than, with increasing preference in the order given, 20, 15, 12, 10, 8.8, 8, 7.5, 7, 6.7, 6.5, 6.3, 6.1, 6, or 5.9 g/l; and

(G) a dissolved accelerator component consisting of at least one substance selected from the group consisting of:

- 0.3 to 4 g/l of chlorate ions;
- 0.05 to 2 g/l ofm-nitrobenzene sulphonate ions;
- 0.05 to 2 g/l of m-nitrobenzoate ions;
- 0.05 to 2 g/l of p-nitrophenol;
- 0.005 to 0.15 g/l of hydrogen peroxide in free or bound form;
- 0.1 to 10 g/l of hydroxylamine in free or bound form; and
- 0.1 to 10 g/l of reducing sugar.

[0029] If the compositions of the first and second zinc phosphate solutions have an initial pH value lower than 3.80 ± 0.03, they have positive Free Acid points which are quantitatively defined as equal to the number of milliliters (hereinafter usually abbreviated as "ml") of 0.100 N strong alkali required to titrate a 10 ml sample of the composition to a pH value of 3.80 ± 0.03. If the initial value of pH of the first and second zinc phosphate solutions is higher than 3.80 ± 0.03, they have negative Free Acid points, which are defined as the negative number with the same absolute value as the number of ml of strong acid required to titrate a 10 ml sample of the composition to a pH of 3.80 ± 0.03. If the first and second zinc phosphate solutions have a pH of 3.80 ± 0.03, they have 0.0 points of Free Acid. In addition to containing the above-noted components, a working composition for the first and second phosphate solutions preferably has a Free Acid value that is at least, with increasing preference in the order given, -1.0, -0.5, 0.0, 0.10, 0.20, 0.30, 0.40, or 0.49 points and independently preferably is not more than, with increasing preference in the order given, 3.0, 2.5, 2.0, 1.90, 1.80, 1.70, 1.60, 1.50, 1.40, 1.30, 1.20, 1.10, 1, 0.9, 0.8, 0.75, 0.7, 0.65, 0.6, or 0.55 points.

[0030] The presence of nickel cations in a composition for the first and second phosphate solutions is preferred, unless the anti-pollution laws where the composition is used make the presence of nickel impractical economically. In such an instance, the presence of copper cations is alternatively preferred, unless they too are economically impractical because of pollution.

[0031] The presence of fluoride containing anions in a composition for the first and second phosphate solutions is generally preferred, especially when phosphating aluminum under most conditions. When phosphating steel or zinciferous surfaces such as galvanized steel, all of the fluoride present is preferably complex fluoride, but when phosphating aluminum, some of the fluoride is preferably present as "free fluoride," a characteristic of the composition that can be measured by a fluoride ion sensitive electrode in contact with the composition and electrically connected to a reference electrode also in the same volume of composition, as known to those skilled in the art. Complex fluoride is preferably supplied to the first and second zinc phosphate solutions by at least one of tetrafluoroboric acid, hexafluorosilicic acid, hexafluorotitanic acid, hexafluorozirconic acid, and salts of all of these acids. At least for economy, hexafluorosilicic acid is most preferred. When free fluoride is needed or desired, it is preferably supplied by hydrofluoric acid and/or ammonium hydrogen fluoride.

[0032] The presence of nitrate in the first and second zinc phosphate solutions is preferred, and independently the nitrate is preferably provided at least in part by nitric acid, although nitrate salts may also be used. When nitrate is used, it preferably is present in a ratio to phosphate that is at least, with increasing preference in the order given, 0.20:1, 0.25:1, 0.30:1, 0.37:1, 0.39:1, 0.41:1, 0.80:1, 1.2:1, 1.6:1, or 1.9:1 and independently, at least for economy, preferably is not more than, with increasing preference in the order given, 30:1, 20:1, 10:1, 5:1, 3:1, 2.5:1, 2.2:1, or 2:1. The major identified reason for a preference for the presence of nitrate in at least the above ratios to phosphate is an improved resistance to corrosion after painting in such tests as GM 9540P, particularly on cold rolled steel.

[0033] Nitrite is used as the accelerator for the first and second phosphate solutions, because of its high technical reliability and effectiveness at a low concentration. When nitrite is used as the accelerator, its concentration preferably is at least 0.2 g/l, and more preferably at least 0.3 g/l. Because nitrite is subject to fairly rapid decomposition in acid solutions, it preferably is not added to a phosphating composition until shortly before it begins to be used and therefore preferably is not included in make-up or replenisher concentrates.

[0034] If the convenience of a single package replenisher is preferred, hydroxylamine in one of its stable bound forms is preferred as the accelerator for the first and second zinc phosphate solutions. Salts of hydroxylamine with any strong acid are generally stable enough in compositions according to the invention to be practically included in single package concentrates, with the sulfate being particularly preferred at least for economy. Oximes can also serve as a suitable source of hydroxylamine. Irrespective of the specific source, when hydroxylamine is used as the accelerator in the first and second zinc phosphate solutions, the concentration, measured as its stoichiometric equivalent as hydroxylamine, preferably is at least, with increasing preference in the order given, 0.20, 0.25, 0.30, 0.33, 0.36, or 0.39 g/l and independently preferably is not more than, with increasing preference in the order given, 1.5, 1.0, 0.90, 0.80, 0.85, 0.80, 0.75, 0.70, 0.65, or 0.61 g/l.

[0035] A phosphating process using either the first or second zinc phosphate solutions can be accomplished by contacting a suitably prepared substrate with either solution. Any method of achieving contact may be used, with one of immersion and spraying generally being preferred, depending on the size and the complexity of the shape of the surface to be phosphated, as generally known in the art. Consistent phosphating results are generally obtained when, and it is therefore preferred that, the temperature of the phosphating composition is controlled while it is in contact with the surface being phosphated. The second zinc phosphate solution preferably operates at low temperatures, preferably between 20°C and 40°C, and more preferably between 30°C and 35°C. The mass of the phosphate coating formed can be determined by methods known in the art. This characteristic of a process according to the invention is generally reported as "coating weight", which is defined as the mass of the coating in g/m^2. For predominantly ferriferous surfaces such as cold rolled steel, the coating weight preferably is at least, with increasing preference in the order given, 0.50, 0.60, 0.70, 0.80, or 0.86 g/m^2 and independently preferably is not more than, with increasing preference in the order given, 5.0, 4.5, 4.0, 3.5, 3.3, 3.0, 2.8, or 2.6 g/m^2. For predominantly zinciferous surfaces such as all types of galvanized steel, the coating weight preferably is at least, with increasing preference in the order given, 0.50, 0.60, 0.70, 0.80, 0.90, 1.00, or 1.10 g/m^2 and independently preferably is not more than, with increasing preference in the order given, 7.0, 6.5, 6.0, 5.5, 5.0, 4.5, 4.1, or 3.8 g/m^2.

[0036] The time of contact between the first and second zinc phosphate solutions and the composite substrate in a process according to the invention is generally not at all critical if the desired coating weight is achieved, presumably because the rate of formation of the coating is much faster at the beginning of contact of a fresh metal surface with the first and second zinc phosphate solutions than after even a thin phosphate coating has initially formed. As a general guideline, when contact is by immersion, the contact time preferably is at least, with increasing preference in the order given, 0.2, 0.5, 0.7, 0.9, 1.1, 1.3, 1.5, 1.7, or 1.9 minutes and independently preferably is not more than, with increasing preference in the order given, 30, 20, 15, 10, 5, 3.0, 2.7, 2.5, 2.3, or 2.1 minutes. When contact is by spraying, the contact time preferably is at least, with increasing preference in the order given, 0.05, 0.10, 0.20, 0.30, 0.40, 0.50, 0.60, 0.70, 0.80, 0.90, or 0.95 minutes and independently preferably is not more than, with increasing preference in the order given, 10, 7, 5, 4.0, 3.5, 3.0, 2.5, or 2.1 minutes.

[0037] Before being contacted with either the first or second zinc phosphate solutions, a composite substrate to be phosphated in a process according to the invention is preferably cleaned, rinsed, and activated by any of the means known for these purposes in the art. Similarly, after the desired time of contact between either the first or second zinc phosphate solutions and a composite substrate has been completed, the substrate is preferably removed from contact with the phosphating composition, rinsed with water, and further treated.

3. Third Type of Zinc Phosphate Solution

[0038] In accordance with a third aspect of the present invention, the third zinc phosphate solution may comprise its low phosphate, high nitrite, and low temperature conditions.

[0039] In accordance with GB 2 199 047 A and the present invention, the third type of zinc phosphate solution contains nitrate, fluoride, less than 5 g/l of phosphate, and 1.5 to 2.5 g/l of zinc. The weight ratio of zinc to phosphate (Zn/PO_4) is preferably 0.08 to 0.21 and the free acidity value is from -0.1 to 0.1 when the amount of zinc is 1.5 g/l, is from 0.1 to 0.5 when the amount of zinc is 2.5 g/l, and is at an interpolated intermediate value at intermediate amounts of zinc. The solution also includes an accelerator, preferably nitrite ions having a concentration of greater than 0.2 g/l and more preferably greater than 0.3 g/l, to accelerate the dissolution of steel from the steel surface and to promote the deposition of Phosphophyllite. With this solution it is possible to obtain good coatings at low temperatures, such as between 20°C and 40°C, and more preferably between 30°C and 35°C.

[0040] Before treatment with the third zinc phosphate solution, the substrate should be cleaned using a conventional cleaning process that is used prior to zinc phosphating. The cleaned surface is also preferably subjected to conventional surface conditioning. The cleaned and conditioned metal surface is then treated with the third zinc phosphate coating solution. Treatment is preferably by dip, conducted preferably at temperatures between 20°C and 40°C, and more preferably between 30°C and 35°C. The third solution is a zinc phosphate coating solution that contains nitrate and fluoride. Particularly important parameters of the solution are its concentration of zinc, the inclusion of an appropriate

amount of an accelerator that is additional to the nitrate that is in the solution, and the relationship between its free acidity and the amount of zinc.

[0041] The amount of zinc is generally above 1.5g/l, which makes it possible to increase the speed of depositing the appropriate phosphate coating on the sheet steel or other surface. If the amount of zinc is less than 1.5g/l, a phosphate coating of the desired weight cannot be formed, and if the amount of zinc is greater than 2.5g/l, the coating becomes too heavy and it is hard to obtain a high P/P+H ratio. Paint film adhesion and corrosion are consequently worse.

[0042] The free acidity chosen is dependent upon the zinc concentration, wherein the optimum free acidity increases as the zinc concentration increases. As a result, the pH of the third zinc phosphate solution can be increased and this broadens the range of conditions at which satisfactory precipitation of zinc phosphate will occur. In particular, the free acidity should be from -0.1 to +0.1 when the amount of zinc is 1.5g/l, should be from 0.1 to 0.5 when the amount of zinc is 2.5 g/l, and at intermediate amounts of zinc the free acidity should be at interpolated intermediate values.

[0043] If the zinc and free acidity values are chosen in the manner indicated, the resultant coating may have an unsatisfactorily low ratio of P/P+H. For instance, the ratio is preferably at least 0.7 and most preferably at least 0.8. A supplemental accelerator is therefore included in order to accelerate the dissolution of iron from the steel surface and to facilitate the deposition of phosphophyllite on to the surface in the coating. In this way the reactivity of the process is such that the resultant phosphate coating gives high quality film performance. In particular, it is preferred to include a nitrite accelerator in an amount of greater than 0.2 g/l of nitrite ions, and more preferably greater than 0.3 g/l of nitrite ions.

[0044] The ratio Zn/PO4 should be between 0.08 and 0.21. If the value is below 0.08 the tendency to form a phosphate coating is seriously worsened, and if the value is above 0.21 there is no advantage, and the crystal size may become too coarse. Preferably the crystal size is mainly in the range of 2 to 5 μm.

[0045] The presence of fluoride contributes to the uniform etching of the steel surface as well as the densification of the phosphate crystals. The fluoride may be introduced as simple fluoride or as complex fluoride. The amount of fluoride is preferably from 0.5 to 1.5g/l. If the amount is below 0.5g/l, etching tends to be non-uniform and densification of the phosphate coating crystals may be poor. If the amount is above 1.5g/l, the phosphate coating tends to become too thin and the performance properties may be difficult to achieve.

[0046] In addition to containing zinc, phosphate, nitrate, fluoride and accelerator, all as described above, it is particularly preferred that the third zinc phosphate solution contain nickel and a small amount of ferrous iron, and manganese.

[0047] The inclusion of nickel contributes to the densification of the phosphate coating crystals and results in improved corrosion resistance and paint adhesion. The amount of nickel is preferably from 0.5 to 1.5g/l. If the amount is below 0.5 g/l, there is inadequate improvement in the density of the phosphate coating crystals, and in the corrosion resistance and paint adhesion. Amounts above 1.5 g/l, are non-economical as they do not provide any improvement.

[0048] Ferrous iron serves to elevate the pH value of the third zinc phosphate solution at which it starts to precipitate, and thus facilitates the formation of the phosphate coating. The amount of ferrous iron is preferably in the range 2 to 20 mg/l. Amounts below 2 mg/l inadequately increase the pH at which precipitation formation occurs, and results in retarded formation of the phosphate coating. If the amount is above 20 m/l, there is a tendency towards the formation of iron phosphate sludge and the destruction of the balance of the treatment solution.

[0049] The inclusion of manganese results in the improvement of the secondary adhesion of the paint film after water soaking and so is particularly preferred when such properties are required. If the amount of Mn^{2+} is above 1 g/l, the formation of the phosphate coating may become harder to achieve and, in particular, its rate of formation may be reduced. If the amount is below 0.2 g/l, there may be no benefit, and so preferably the amount of manganese is from 0.2 to 1 g/l.

[0050] The preferred process using the third zinc phosphate solution is for the formation of a phosphate conversion coating on composite structures which have been cleaned and surface conditioned. In this process the composite structures are dip-treated with the third zinc phosphate solution containing less than 5 g/l of phosphate ions, 5 to 15 g/l nitrate, 0.5 to 1.5 g/l fluorine compound, 0.5 to 1.5 g/l divalent nickel, 2 to 20 mg/l trivalent iron, and 1.5 to 2.5g/l divalent zinc, and the weight ratio of zinc to phosphate is 0.08 to 0.21. Since the free acid is dependent on the concentration of zinc, the third zinc phosphate solution contains a nitrite accelerator at a concentration of greater than 0.2 g/l of nitrite ions, and the process is conducted at a temperature of 15 to 39°C, or at 20 to 30 or 35 °C. The dip treatment is generally conducted for between 0.5 to 3 minutes.

[0051] The aluminum may be precleaned with compositions and a preclean process, as described in, US Statutory Invention Registration US H2089 H entitled COMPOSITIONS USEFUL FOR DEGREASING METAL SURFACES, the disclosure of which is herein incorporated by reference. If the aluminum being treated by the process and compositions of the present invention is difficult to clean and the precleaning compositions and process of US H2089 H is incapable of cleaning the aluminum, then the first step of the process of the present invention may also be used to etch (oxidize) the aluminum to prepare it for the second step of the process and to remove any remaining grease, soil, oxides, etc. on the aluminum surface.

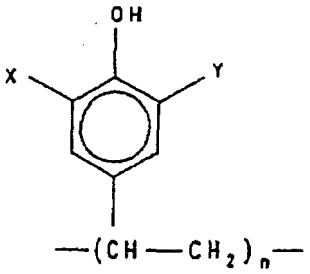
B. **The Second Process Step**

[0052] The second step (II) imparts corrosion protection to the aluminum while not reducing, and preferably improving, the corrosion prevention properties of the zinc-phosphated steel or zinc.

[0053] In accordance with WO 99/12661 and the present invention, in step (II), solutions according to the prior art that produce a conversion layer on aluminum may be used. These solutions must not, however, excessively dissolve the crystalline zinc phosphate layer formed in step (I). The pH of these solutions should therefore lie in the range from 3.3 to 10. Advantageously, in step (II), solutions are chosen containing components that additionally passivate the crystalline zinc phosphate layers. Such solutions are mentioned hereinafter by way of example. In step (II), the metal structures are generally brought into contact with the treatment solutions by spraying or by dipping. The temperature of the treatment solution for step (II) is preferably chosen in the range from 20 to 70°C.

[0054] By way of example, in step (II) a treatment solution may be used that has a pH in the range from about 5 to about 5.5 and that contains overall about 0.3 to about 1.5 g/l of hexafluorotitanate and/or hexafluorozirconate ions. It may be advantageous for the corrosion protection of the crystalline zinc phosphate layer produced in step (I) if this treatment solution additionally contains about 0.01 to 0.1 g/l of copper ions for step (II)

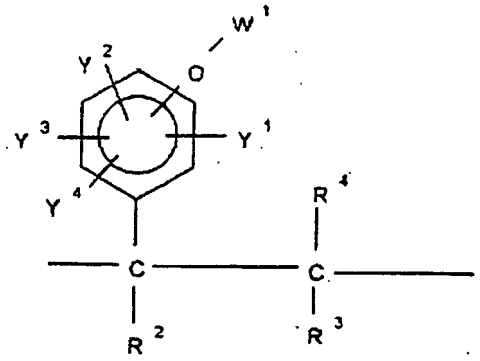
[0055] Moreover, a treatment solution may be used in step (II) that has a pH in the range from 3.5 to 5.8 and that contains 10 to 500 mg/l of organic polymers chosen from poly-4-vinylphenol compounds of the immediately following general formula (I):



wherein n is an integer between 5 and 100, each of X and Y independently of each other denotes hydrogen or a CRR^1OH moiety in which each of R and R^1 independently is hydrogen or an aliphatic or aromatic moiety with 1 to 12 carbon atoms.

[0056] For step (II) in particular those treatment solutions are preferred that contain polyvinylphenol derivatives according to the teaching of **European Patent No.** 0 319 016 B1**.** This document also discloses the preparation of such polyvinylphenol derivatives. Accordingly, in step (II) a treatment solution is preferably used that has a pH in the range from 3.3 to 5.8 and contains 10 to 5000 mg/l of organic polymers selected from homopolymer or copolymer compounds containing amino groups, comprising at least one polymer selected from the group consisting of materials (α) and (β), wherein:

(α) consists of polymer molecules each of which has at least one unit conforming to the immediately following general formula (II):

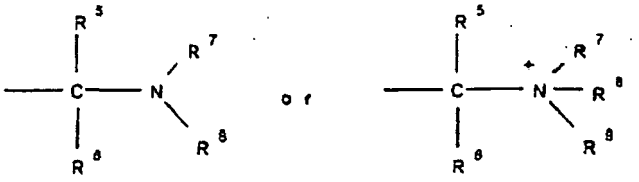


wherein:

- each of R^2 through R^4 is selected, independently of each other and independently from one molecule of the

component to another and from one to another unit of any polymer molecule conforming to this formula when there is more than one such unit in a single polymer molecule,
from the group consisting of a hydrogen moiety, an alkyl moiety with from 1 to 5 carbon atoms, and an aryl moiety with from 6 to 18 carbon atoms;

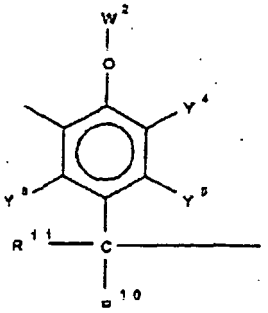
- each of Y^1 through Y^4 is selected, independently of each other and S independently from one molecule of the component to another and from one to another unit of any polymer molecule conforming to this formula when there is more than one such unit in a single polymer molecule, except as noted further below, from the group consisting of: a hydrogen moiety; a $-CH_2Cl$ moiety; an alkyl moiety with from 1 to 18 carbon atoms; an aryl moiety with from 6 to 18 carbon atoms; a moiety conforming to the general formula $-CR^{12}R^{13}OR^{14}$, where each of R^{12} through R^{14} is selected from the group consisting of a hydrogen moiety, an alkyl moiety, an aryl moiety, a hydroxyalkyl moiety, an aminoalkyl moiety, a mercaptoalkyl moiety, and a phosphoalkyl moiety; and a moiety Z that conforms to one of the two immediately following general formulas:



where each of R^5 through R^8 is selected, independently of each other and independently from one molecule of the component to another and from one to another unit of any polymer molecule conforming to this formula when there is more than one such unit in a single polymer molecule, from the group consisting of a hydrogen moiety, an alkyl moiety, an aryl moiety, a hydroxyalkyl moiety, an aminoalkyl moiety, a mercaptoalkyl moiety, and a phosphoalkyl moiety and R^9 is selected from the group consisting of a hydrogen moiety, an alkyl moiety, an aryl moiety, a hydroxy or polyhydroxy alkyl moiety, an amino or polyamino alkyl moiety, a mercapto or polymercapto alkyl moiety, a phospho or polyphospho alkyl moiety, an -0 moiety, and an -OH moiety,

- at least one of Y^1 through Y^4 in at least one unit of each selected polymer 35 molecule being a moiety Z as above defined; and
- W^1 is selected, independently from one molecule of the component to another and from one to another unit of any polymer molecule conforming to this formula when there is more than one such unit in a single polymer molecule, from the group consisting of a hydrogen moiety, an acyl moiety, an acetyl moiety, a benzoyl moiety; a 3-allyloxy-2-hydroxypropyl moiety; a 3-benzyloxy-2-hydroxypropyl moiety; a 3-butoxy-2-hydroxypropyl moiety; a 3-alkyloxy-2-hydroxypropyl moiety; a 2-hydroxyoctyl moiety; a 2-hydroxyalkyl moiety; a 2-hydroxy-2-phenylethyl moiety; a 2-hydroxy-2-alkylphenylethyl moiety; a benzyl, methyl, ethyl, propyl,

unsubstituted alkyl, unsubstituted allyl, unsubstituted alkylbenzyl; halo or polyhalo alkyl, or halo or poly haloalkenyl moiety; a moiety derived from a condensation polymerization product of ethylene oxide, propylene oxide or a mixture thereof by deleting one hydrogen atom therefrom; and a sodium, potassium, lithium, ammonium or substituted ammonium, or phosphonium or substituted phosphonium cation moiety; and
(β) consists of polymer molecules each of which does not include a unit conforming to general formula (II) as given above but does include at least one unit corresponding to the immediately following general formula (III):



wherein:

- each of R^{10} and R^{11} is selected, independently of each other and independently from one molecule of the component to another and from one to another unit of any polymer molecule conforming to this formula when there is more than one such unit in a single polymer molecule, from the group consisting of a hydrogen moiety, an alkyl moiety with from 1 to 5 carbon atoms, and an aryl moiety with from 6 to 18 carbon atoms;
- each of Y^4 through Y^6 is selected, independently of each other and independently from one molecule of the component to another and from one to another unit of any polymer molecule conforming to this formula when there is more than one such unit in a single polymer molecule, except as noted further below, from the group consisting of: a hydrogen moiety; a $-CH_2Cl$

moiety; an alkyl moiety with from I to 18 carbon atoms; an aryl moiety with from 6 to 18 carbon atoms; a moiety conforming to the general formula $-CR^{12}R^{13}OR^{14}$, where each of R^{12} through R^{14} is selected from the group consisting of a hydrogen moiety, an alkyl moiety, an aryl moiety, a hydroxyalkyl moiety, an aminoalkyl moiety, a mercaptoalkyl moiety, and a phosphoalkyl moiety; and a moiety Z as defined for material (a) above, at least one of Y^1 through Y^4 in at least one unit of each selected polymer molecule being a moiety Z as above defined; and - W^2 is selected, independently from one molecule of the component to another and from one to another unit of any polymer molecule conforming to this formula 15 when there is more than one such unit in a single polymer molecule, from the group consisting of a hydrogen moiety, an acyl moiety, an acetyl moiety, a benzoyl moiety; a 3-allyloxy-2-hydroxypropyl moiety; a 3-benzyloxy-2-hydroxypropyl moiety; a 3-butoxy-2-hydroxypropyl moiety; a 3-alkyloxy-2-hydroxypropyl moiety; a 2-hydroxyoctyl moiety; a 2-hydroxyalkyl moiety; a 2-hydroxy-2-phenylethyl moiety; a 2-hydroxy-2-alkylphenylethyl moiety; a benzyl, methyl, ethyl, propyl, unsubstituted alkyl, unsubstituted alkyl, unsubstituted alkylbenzyl; halo or polyhalo alkyl, or halo or polyhalo alkenyl moiety; a moiety derived from a condensation polymerization product of ethylene oxide, propylene oxide or a mixture thereof by deleting one hydrogen atom therefrom; and a sodium, potassium, lithium, ammonium or substituted ammonium, or phosphonium or substituted phosphonium cation moiety;

[0057] The phrase "polymer molecule" in the above definitions of materials (α) and (β) including any electrically neutral molecule with a molecular weight of at least 300 daltons.

[0058] Ordinarily, primarily for reasons of economy, it is preferred to utilize as materials 30 (α) and/or (β) predominantly molecules which consist entirely, except for relatively short end groups, of units conforming to one of the general formulas (I) and (II) as described above. Again primarily for reasons of economy, such materials are generally prepared by reacting homopolymers of p-vinyl phenol, for material (α), or phenol-aldehyde condensation products, for material with formaldehyde and secondary amines to graft moieties Z on some of the activated benzene rings in the materials thus reacted.

[0059] However, in some particular instances, it may be more useful to utilize more chemically complex types of materials (α) and/or (β). For example, molecules formed by reacting a condensable form of a molecule belonging to component (α) or (β) as defined above, except that the molecule reacted need not initially satisfy the requirement for component (α) or (β) that each molecule contain at least one moiety Z, with at least one other distinct type of molecule which is selected from the group consisting of phenols, tannins, novolak resins, lignin compounds, aldehydes, ketones, and mixtures thereof, in order to prepare a condensation reaction product, which optionally if needed is then further reacted with (1) an aldehyde or ketone and (2) a secondary amine to introduce at least one moiety Z as above defined to each molecule, so that the molecule can qualify as material (α) or (β).

[0060] Another example of more complex materials that can be utilized as material (α) is a material in which the polymer chains are at least predominantly copolymers of simple or substituted 4-vinyl phenol with another vinyl monomer such as acrylonitrile, metha-crylonitrile, methyl acrylate, methyl methacrylate, vinyl acetate, vinyl methyl ketone, isopropenyl methyl ketone, acrylic acid, methacrylic acid, acrylamide, methacrylamide namyl methacrylate, styrene, n-bromostyrene, p-bromostyrene, pyridine, diallyldimethylammonium salts, 1,3-butadiene, n-butyl acrylate, t-butylamino-ethyl methacrylate, n-butyl methacrylate, t-butyl methacrylate n-butyl vinyl ether, t-butyl vinyl ether, m-chlorostyrene, p-chlorostyrene, p-chlorostyrene, n-decyl methacrylate, N,N-diallylmelamine, N,N-di-n-butylacrylamide, di-n-butyl itaconate, di-n-butyl maleate, diethylaminoethyl methacrylate, diethylene glycol monovinyl ether, diethyl fumarate, diethyl itaconate, diethylvinyl phosphate, vinylphosphonic acid, diisobutyl maleate, diisopropyl itaconate, diisopropyl maleate, dimethyl fumarate, dimethyl itaconate, dimethyl maleate, di-n-nonyl fumarate, di-n-nonyl maleate, dioctyl fumarate, di-n-octyl itaconate di-n-propyl itaconate, N-dodecyl vinyl ether, acidic ethyl fumarate, acidic ethyl maleate, ethyl acrylate, ethyl cinnamate, N-ethyl methacrylamide, ethyl methacrylate, ethyl vinyl ether, 5-ethyl-2-vinylpyridine, 5-ethyl-2-vinylpyridine-1 -oxide, glycidyl acrylate, glycidyl methacrylate, n-hexyl methacrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methacrylate, isobutyl methacrylate, isobutyl vinyl ether, isoprene, isopropyl methacrylate, isopropyl vinyl ether, itaionic acid, lauryl methacrylate, methacrylamide, methacrylic acid, methacrylonitrile, N-methylolacrylamide, N-methylol-methacrylamide, N-isobutoxymethylacrylamide, N-isobutoxy-methylmethacrylamide, N-alkyloxymethylacrylamide, N-alkyloxymethylmethacrylamide, N-vinylcaprolactam, methyl acrylate, N-methylmethacrylamide, a-methylstyrene, n-methylstyrene, a-methyl styrene, p-methylstyrene, 2-methyl-5-vinylpyridine, n-propyl methacrylate, sodium p-styrenesulfonate,

stearyl methacrylate, styrene, p-styrenesulfonic acid, p-styrenesulfonamide, vinyl bromide, 9-vinyl carbazole, vinyl chloride, vinylidene chloride, 1-vinylnaphthalene, 2-vinylnaphthalene, 2-vinylpyridine, 4-vinylpyridine, 2-vinylpyridine N-oxide, 4-vinylpyrimidine, and N-vinylpyrrolidone.

[0061] The following preferences, primarily for reasons of economy, improve corrosion resistance, and/or increase water solubility, apply, independently for each preference, to the molecules of materials (α) and (β):

each of R^2 through R^6, R^{10}, R^{11}, W^1, and W^2, independently for each and from one unit to another in the same or a different molecule, preferably is a hydrogen moiety;

- each of Y^1 through Y^6, independently for each and from one unit to another in the same or a different molecule, preferably is a hydrogen moiety or a moiety Z;
- each polymer molecule contains a number of units corresponding to one of general formulas (II) and (III) as defined above that is at least, with increasing preference in the order given, 2, 3, 4, 5, 6, 7, or 8 and independently preferably is not more than 100, 75, 50, 40, 30, or 20;
- in the total of materials (α) and (β) in a composition used in step (II) according to the invention, the number of moieties Z has a ratio to the number of aromatic nuclei that is at least, with increasing preference in the order given, 0.01:1.0, 0.03:1.0, 0.05:1.0, 0.10:1.0, 0.20:1.0, 0.40:1.0, 0.50:1.0, 0.60:1.0, 0.70:1.0, 0.80:1.0, 0.90:1.0, or 0.95:1.0, and independently preferably is not more than, with increasing preference in the order given, 2.0:1.0, 1.6:1.0, 1.50:1.0, 1.40:1.0, 1.30:1.0, 1.20:1.0, 1.10:1.0, or 1.00:1.0; and
- in the total of materials (α) and (β) in a composition used in step (II) according to the invention, the number of "polyhydroxy moieties Z", which are defined as moieties Z in which at least one of R^5 through R^8 in the general formulas given above for moieties Z has (i) from 3 to 8, or preferably from 4 to 6, carbon atoms and (ii) as many hydroxyl groups, each attached to one of the carbon atoms, as one less than the number of carbon atoms in the R^5 through R^8 moiety, has a ratio to the total number of moieties Z in the composition that is at least, with increasing preference in the order given, 0.10:1.0, 0.20:1.0, 0.30:1.0, 0.40:1.0, 0.50:1.0, 0.60:1.0, 0.70:1.0, 0.80:1.0, 0.90:1.0, or 0.98:1.0 (preparation of such materials is described in the references cited above).

[0062] Poly(5-vinyl-2-hydroxy-N-benzyl)-N-methylglucamine is a specific polymer of the most preferred type, which, in the acidic pH range which is to be established, is present at least in part as an ammonium salt.

[0063] Solutions may be used that do not contain any further active constituents, apart from the polyvinyl phenol derivative and an acid for adjusting the pH, preferably phosphoric acid. Additions of further active constituents, in particular hexafluorotitanate or hexafluorozirconate ions, may however improve the layer formation on aluminum. For example, a solution may be used whose pH lies preferably in the range from about 3.3 to about 5.8 and which contains as organic polymer about 100 to about 5000 mg/l of an organic polymer in the form of a methylethanolamine derivative or N-methylglucamine derivative of polyvinyl phenol and in addition 10 to 2000 mg/l of phosphate ions, 10 to 2500 mg/l of hexafluorotitanate or hexafluorozirconate ions, and 10 to 1000 mg/l of manganese ions.

[0064] Instead of the polyvinyl phenol derivatives, whose preparation involves a certain expense, there may be used in step (II) solutions or dispersions of organic polymers selected from homopolymers and/or copolymers of acrylic acid and methacrylic acid as well as their esters. Preferably these solutions or dispersions have pH values in the range from about 3.3 to about 4.8 and contain about 250 to about 1500 mg/l of organic polymers. According to the teaching of **European Patent** 0 08 942 B1 these polymer solutions or dispersions may additionally contain hexafluorotitanates, hexafluorozirconates and/or hexafluorosilicates.

[0065] The two-step process of the present invention provides a chemical pretreatment, before an organic coating, of composite metal structures that contain aluminum, zinc, and steel in any ratio. The low phosphate ion concentration (less than 5 g/l), and high nitrite concentration (greater than 0.2 g/l) reduces the need for monitoring the process, and reduces the sludge produced during the first step of the process, reducing the environmental impact of the process. The low temperature operation (less than 40 °C) of the first step of the process reduces the energy consumed by the process, providing cost savings. Furthermore, the pretreatment process of the present invention forms a conversion layer on all exposed zinc, steel, and aluminum surfaces that is suitable as a corrosion-preventing paint substrate, especially before a cathodic electro-dipcoating.

EXAMPLES

[0066] A process sequence according to the invention was tested on sample metal sheets (four inch by four inch panels) of cold rolled steel (hereinafter abbreviated as "CRS"), aluminum 6111 ("A1 6111 "), eletrolytically galvanized steel (hereinafter abbreviated as "EG steel"), and hot dip galvanized steel (hereinafter abbreviated as "HDG steel"). As is conventional in the automobile manufacturing sector, the metal sheets were first cleaned with alkali and activated with an activating solution containing titanium phosphate, and then rinsed with deionized water. The metal sheets were then dipped in a phosphating bath for 120 seconds. The general process cycle for the samples is shown below as Table 1.

The composition of the phosphate solution used for the samples is shown below in Table 2, and a theoretical composition of the phosphate solution is shown below as Table 3. Table 4 shows examples of the substrate metal loss and phosphate coating weight for samples exposed to the phosphating process of the present invention. Table 5 shows examples of the weight loss on phosphated samples due to post-treatments.

Table 1

					Process		
		Titanium (ppm)			(°C) [(°F)]	(sec.)	Application Method
Material	**Concentration**	Total	Filterable	pH	Temperature	Time	
Parco Cleaner 1533	Free Alkali = 5.9 points, Total Alkali = 6.8 points			12	49 [120]	90	spray
Warm Tap Water					32 [~90]	30	spray
Fixodine ZL	3 g/l (titanium phosphate containing compound)	9	6	9.3	ambient	30	spray
Phosphate	See Phosphating Process Examples					120	dip
Cold Tap Water					16 [-60]	30	spray
Post treatment "A"	1.59 g/l H_2ZrF_6 (45%)			4.12	ambient	30	spray
	or						
Post treatment "B"	250 ppm H_2ZrF_6 (45%), 400 ppm organic polymer*			4.23	ambient	30	spray
Deionized Water					ambient	30	spray
*Polyvinylphenol derivative							

Table 2

	Phosphating Solution Composition (g/l)										Operating Parameters	
Process Number	ZnO	$Ni_3(PO_4)_2$ soln. (8.25% Ni, 37.6% PO_4)	MnO	H_3PO_4 (75% w/w)	HNO_3 (67% w/w)	H_2SiF_6 (25% w/w)	$NaNO_2$	NaOH soln. (19.8% w/w)	$FeSO_4 \cdot 7H_20$	Free Fluoride	Free Acid* points, 10 ml	Temp. (°C) [(°F)]
1*	1.24	6.1	0.52	3.1	6.8	2	0.11	13.6	0.16		0.7	49 [120]
	$Zn(NO_3)_2$ soln. (50%w/w)	$Ni(NO_3)_2$ soln. (26%w/w)	$Mn(NO_3)_2$ soln. (30%w/w)									
2	10.8	3.45	2.85	4.1	1	5.1	0.45	12.3		0.038	0.2	27 [80]
3	10.8	3.45	2.85	4.1	1.2	5.1	0.46	12.3		0.027	0.6	27 [80]
4	10.8	3.45	2.85	4.1	1.4	5.1	0.47	12.3		0.019	0.8	26 [79]
5	11.1	3.45	2.55	4.1	1	5.1	0.46	12.9		0.039	0.3	32 [90]
6	11.1	3.45	2.55	4.1	1.2	5.1	0.46	12.9		0.024	0.5	32 [90]
7	11.1	3.45	2.55	4.1	1.4	5.1	0.48	12.9		0.020	0.7	32 [90]
* comparative example												

Table 3

Process Number	Theoretical Phosphating Solution Composition (g/l)							
	Phosphate	Fluoride	Manganese	Zinc	Nickel	Nitrate	Nitrite	Sodium
1	4.5	0.4	0.40	1.00	0.50	4.46	0.07	1.55
2	3	1	0.26	1.86	0.29	5.43	0.30	1.59
3	3	1	0.26	1.86	0.29	5.56	0.31	1.59
4	3	1	0.26	1.86	0.29	5.69	0.31	1.59
5	3	1	0.23	1.91	0.29	5.47	0.31	1.66
6	3	1	0.23	1.91	0.29	5.60	0.31	1.66
7	3	1	0.23	1.91	0.29	5.73	0.32	1.67
* comparative example								

Table 4

Example Number	Process Number	Substrate	Clean Wt. (g)	Coated Wt. (g)	Stripped Wt. (g)	Ct. Wt. (g/m^2)	Wt. Loss (g/m^2)
1	1	Al 6111	25.302	25.293	25.29	0.15	0.58
2	1	Al 6111	25.903	25.889	25.89	-0.05	0.63
7	2	Al 6111	38.101	38.096	38.088	0.26	0.42
8	2	Al 6111	37.846	37.835	37.827	0.26	0.61
9	3	Al 6111	38.047	38.036	38.035	0.03	0.39
10	3	Al 6111	38.037	38.029	38.028	0.03	0.29
11	4	Al 6111	37.703	37.695	37.694	0.03	0.29
12	4	Al 6111	38.250	38.245	38.245	0.00	0.16
13	5	Al 6111	38.671	38.660	38.658	0.06	0.42
14	5	Al 6111	38.659	38.659	38.654	0.16	0.16
15	6	Al 6111	37.844	37.850	37.840	0.32	0.13
16	6	Al 6111	37.728	37.732	37.721	0.36	0.23
17	7	Al 6111	38.658	38.654	38.651	0.10	0.23
18	7	Al 6111	37.499	37.495	37.492	0.10	0.23
19	1	CRS	63.978	64.020	63.956	3.10	1.07
20	1	CRS	67.042	67.083	67.024	2.86	0.87
21	2	CRS	98.676	98.748	98.651	3.13	0.81
22	2	CRS	99.198	99.277	99.18	3.13	0.58
23	3	CRS	99.639	99.677	99.6	2.49	1.26
24	3	CRS	99.258	99.311	99.224	2.81	1.10
25	4	CRS	99.403	99.453	99.379	2.39	0.77
26	4	CRS	99.004	99.055	98.982	2.36	0.71
27	5	CRS	100.439	100.512	100.418	3.04	0.68

(continued)

Example Number	Process Number	Substrate	Clean Wt. (g)	Coated Wt. (g)	Stripped Wt. (g)	Ct. Wt. (g/m^2)	Wt. Loss (g/m^2)
28	5	CRS	97.654	97.718	97.634	2.71	0.65
29	6	CRS	99.284	99.351	99.271	2.58	0.42
30	6	CRS	98.237	98.304	98.226	2.52	0.36
31	7	CRS	98.857	98.902	98.841	1.97	0.52
32	7	CRS	96.636	96.685	96.624	1.97	0.39
33	1	EG	61.845	61.871	61.825	2.23	0.97
34	1	EG	63.458	63.484	63.437	2.28	1.02
35	2	EG	93.791	93.844	93.743	3.26	1.55
36	2	EG	93.474	93.526	93.44	2.78	1.10
37	3	EG	94.198	94.241	94.159	2.65	1.26
38	3	EG	92.17	92.211	92.13	2.62	1.29
39	4	EG	94.778	94.82	94.734	2.78	1.42
40	4	EG	93.599	93.639	93.555	2.71	1.42
41	5	EG	93.147	93.2	93.116	2.71	1.00
42	5	EG	92.237	92.289	92.204	2.74	1.07
43	6	EG	94.841	94.9	94.826	2.39	0.48
44	6	EG	93.832	93.884	93.811	2.36	0.68
45	7	EG	93.029	93.063	92.997	2.13	1.03
46	7	EG	93.99	94.031	93.963	2.20	0.87
47	2	HDG	95.041	95.083	95.004	2.55	1.19
48	2	HDG	95.74	95.79	95.71	2.58	0.97
49	3	HDG	93.981	94.023	93.94	2.68	1.32
50	3	HDG	98.741	98.789	98.696	3.00	1.45
51	4	HDG	106.568	106.612	106.52	2.97	1.55
52	4	HDG	107.082	107.124	107.031	3.00	1.65
53	5	HDG	94.818	94.875	94.785	2.91	1.07
54	5	HDG	95.844	95.905	95.811	3.04,	1.07
55	6	HDG	95.102	95.148	95.08	2.20	0.71
56	6	HDG	96.265	96.315	96.239	2.45	0.84
57	7	HDG	94.714	94.75	94.678	2.32	1.16
58	7	HDG	96.68	96.722	96.649	2.36	1.00

Table 5

Phosphate Process Number		Weight Loss due to Post Treatment			
		Post treatment "A"		Post treatment "B"	
	Substrate	grams	g/m^2	grams	g/m^2
2	Al 6111	0.003	0.15	0.000	0.00
2	CRS	0.004	0.19	0.000	0.00
2	EG	0.004	0.19	0.000	0.00
2	HDG	0.003	0.15	0.000	0.00
3	Al 6111	0.002	0.10	0.000	0.00
3	CRS	0.002	0.10	0.001	0.05
3	EG	0.001	0.05	0.000	0.00
3	HDG	0.004	0.19	0.002	0.10
4	Al 6111	0.001	0.05	0.000	0.00
4	CRS	0.001	0.05	0.001	0.05
4	EG	0.003	0.15	0.000	0.00
4	HDG	0.002	0.10	0.001	0.05
5	Al 6111	0.002	0.10	0.000	0.00
5	CRS	0.002	0.10	0.001	0.05
5	EG	0.002	0.10	0.001	0.05
5	HDG	0.002	0.10	0.001	0.05
6	Al 6111	0.001	0.05	0.000	0.00
6	CRS	0.003	0.15	0.002	0.10
6	EG	0.002	0.10	0.001	0.05
6	HDG	0.002	0.10	0.002	0.10
7	Al 6111	0.002	0.10	0.000	0.00
7	CRS	0.001	0.05	0.000	0.00
7	EG	0.000	0.00	0.000	0.00
7	HDG	0.000	0.00	0.000	0.00

[0067] Where in Table 5, the panels were treated for 30 seconds with the following post-treatments:

(1) Post Treatment "A" = DY58AL; Concentration = 15.6 points = 1.59 g/l H_2ZrF_6 (45%); pH = 4.12; and
(2) Post Treatment "B" = TD1355CN/H2ZrF6; Organic polymer = 400 PPM = 1350 PPM TD1355CN = polyvinylphenol derivative; Zirconium = 50 PPM = 250 PPM H_2ZrF_6 (45%); and pH = 4.23.

Claims

1. A process for chemical pretreatment, before an organic coating, of a composite metal structure that contains at least one aluminum or aluminum alloy portion, at least one zinc or zinc alloy portion, and at least one steel, galvanized steel or alloy-galvanized steel portion, the process comprising:

(I) treating the composite metal structure with a zinc phosphating solution having less than 5 g/l of phosphate ions and more than 0.2 g/l of nitrite ions, the zinc phosphating solution forming a surface-covering crystalline zinc phosphate layer having a coating weight in the range from 0.5 to 5 g/m^2 on the zinc or zinc alloy, steel,

galvanized steel, or alloy-galvanized steel portions, but without forming a zinc phosphate layer on the aluminum or aluminum alloy portion; and
(II) subsequently, contacting the composite metal structure with a treatment solution with a pH in the range from 3.3 to 10 which does not dissolve more than 60 % of the crystalline zinc phosphate layer formed during step (I) on the zinc or zinc alloy, steel, galvanized steel, or alloy-galvanized steel portions, but does produce a conversion layer on the aluminum or aluminum alloy portion,

wherein the zinc phosphating solution used in step (I) further comprises:

a) 0.30 to 3.0 g/l of zinc cations;
b) 0.05 to 2.0 g/l of manganese(II) cations;

wherein the zinc phosphating solution used in step (I) has a Free Acid value of 1.0 to 3.0 points and a concentration of free fluoride ions in the zinc phosphating solution according to process step (I), measured in g/l, at a specific temperature T (in °C) that is below a value of 8/T.

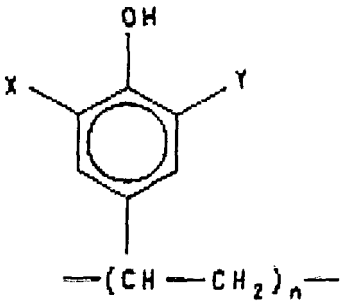
2. A process as recited in claim 1, wherein the zinc phosphating solution used in step (I) has a temperature in a range from 20°C to 40°C; and in step (II) the treatment solution does not dissolve more than 25 %, preferably not more than 10 % of the crystalline zinc phosphate layer deposited in step (I).

3. A process as recited in claim 1 or 2, wherein in step (I) the zinc phosphating solution has a temperature in a range from 30°C to 35 °C.

4. A process as recited in one or more of claims 1 to 3, wherein the treatment solution used in step (II) has a pH in a range from 3.3 to 5.5 and comprises from 0.3 to 1.5 g/l of one of hexafluorotitanate ions, hexafluorozirconate ions, or both.

5. A process as recited in one or more of claims 1 to 4, wherein the treatment solution used in step (II) further includes from 0.01 to 0.1 g/l of copper ions.

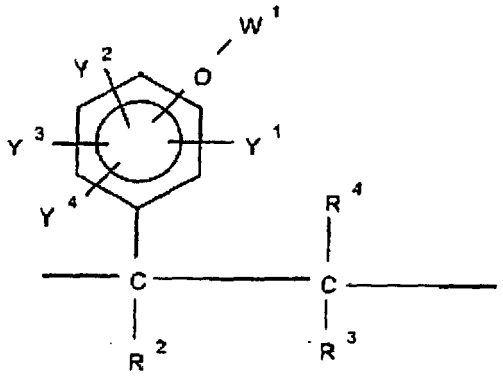
6. A process as recited in one or more of claims 1 to 3, wherein the treatment solution used in step (II) has a pH in a range from 3.5 to 5.8 and contains from 10 to 500 mg/l of organic polymers selected from poly-4-vinylphenol molecules that conform to the general formula (I):



(I)

wherein n is an integer between 5 and 100, each of X and Y independently of each other denotes hydrogen or a CRR^1OH moiety in which each of R and R^1 independently is hydrogen or an aliphatic or an aromatic moiety with 1 to 12 carbon atoms.

7. A process as recited in one or more of claims 1 to 3, wherein the treatment solution used in step (II) has a pH in a range from 3.3 to 5.8 and contains from 10 to 5000 mg/l of organic polymers each of which has at least one unit conforming to the general formula (II):

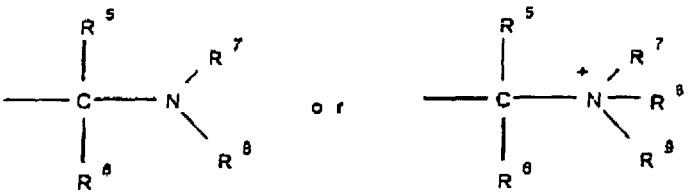


(II)

wherein:

- each of R^2 through R^4 is selected, independently of each other and independently from one molecule of the component to another and from one to another unit of any polymer molecule conforming to this formula when there is more than one such unit in a single polymer molecule, from the group consisting of a hydrogen moiety, an alkyl moiety with from 1 to 5 carbon atoms, and an aryl moiety with from 6 to 18 carbon atoms;
- each of Y^1 through Y^4 is selected, independently of each other and independently from one molecule of the component to another and from one to another unit of any polymer molecule conforming to this formula when there is more than one such unit in a single polymer molecule, except as noted further below, from the group consisting of: a hydrogen moiety; a $-CH_2Cl$ moiety; an alkyl moiety with from 1 to 18 carbon atoms; an aryl moiety with from 6 to 18 carbon atoms; a moiety conforming to the general formula $-CR^{12}R^{13}OR^{14}$, where each of R^{12} through R^{14} is selected from the group consisting of a hydrogen moiety, an alkyl moiety, an aryl moiety, a hydroxyalkyl moiety, an aminoalkyl moiety, a mercaptoalkyl moiety, and a phosphoalkyl moiety;

and a moiety Z that conforms to one of the two immediately following general formulas:



- where each of R^5 through R^8 is selected, independently of each other and independently from one molecule of the component to another and from one to another unit of any polymer molecule conforming to this formula when there is more than one such unit in a single polymer molecule, from the group consisting of a hydrogen moiety, an alkyl moiety, an aryl moiety, a hydroxyalkyl moiety, an aminoalkyl moiety, a mercaptoalkyl moiety, and a phosphoalkyl moiety; and
R^9 is selected from the group consisting of a hydrogen moiety, an alkyl moiety, an aryl moiety, a hydroxy or polyhydroxy alkyl moiety, an amino or polyamino alkyl moiety, a mercapto or polymercapto alkyl moiety, a phospho or polyphospho alkyl moiety, an -0 moiety, and an -OH moiety,
- at least one of Y^1 through Y^4 in at least one unit of each selected polymer molecule being a moiety Z as above defined; and
- W^1 is selected, independently from one molecule of the component to another and from one to another unit of any polymer molecule conforming to this formula when there is more than one such unit in a single polymer molecule, from the group consisting of a hydrogen moiety, an acyl moiety, an acetyl moiety, a benzoyl moiety; a 3-allyloxy-2-hydroxypropyl moiety; a 3-benzyloxy-2-hydroxypropyl moiety; a 3-butoxy-2-hydroxypropyl moiety; a 3-alkyloxy-2-hydroxypropyl moiety; a 2-hydroxyoctyl moiety; a 2-hydroxyalkyl moiety; a 2-hydroxy-2-phenylethyl moiety; a 2-hydroxy-2-alkylphenylethyl moiety; a benzyl, methyl, ethyl, propyl, unsubstituted alkyl, unsubstituted allyl, unsubstituted alkylbenzyl; halo or polyhalo alkyl, or halo or poly haloalkenyl moiety; a moiety derived from a condensation polymerization product of ethylene oxide, propylene oxide or a mixture thereof by

deleting one hydrogen atom therefrom; and a sodium, potassium, lithium, ammonium or substituted ammonium, or phosphonium or substituted phosphonium cation moiety.

8. A process as recited in claim 7, wherein the organic polymer that consists of units according to the general formula (II) is selected from condensation reaction products of:

i) polyvinyl phenol;
ii) formaldehyde; and
iii)at least one secondary organic amine.

9. A process as recited in claim 8, wherein the organic polymer that consists of units according to the general formula (II) is poly(5-vinyl-2-hydroxy-N-benzyl)-N-methylglucamine.

10. A process as recited in one or more of claims 6 to 9, wherein the treatment solution used in step (II) further comprises hexafluorotitanate and/or hexafluorozirconate ions.

11. A process as recited in one or more of claims 1 to 3, wherein the treatment solution used in step (II) has a pH in a range from 3.3 to 5.8 and contains:

i) 100 to 5000 mg/l of an organic polymer in the form of a methylethanolamine derivative or N-methylglucamine derivative of polyvinyl phenol according to claim 9;
ii) 10 to 2000 mg/l of phosphate ions;
iii) 10 to 2500 mg/l of hexafluorotitanate ions, hexafluorozirconate ions, or both; and
iv) 10 to 1000 mg/l of manganese ions.

12. A process as recited in one or more of claims 1 to 3, wherein the treatment solution used in step (II) has a pH in the range from 3.3 to 4.8 and comprises from 250 to 1500 mg/l of organic polymers selected from the group consisting of homopolymers and copolymers of acrylic acid, methacrylic acid, and esters of acrylic and methacrylic acids.

13. A process as recited in claim 12, wherein the treatment solution used in step (II) further comprises hexafluorotitanate, hexafluorozirconate and/or hexafluorosilicate ions.

14. A process as recited in one or more of claims 1 to 13, wherein the zinc phosphating solution used in step (I) comprises 0.30 to 2.0 g/l of zinc cations and further comprises at least one or more of:

c) 0.1 to 2.0 g/l of nickel(II) cations;
d) 0.0001 to 0.03 g/l of copper cations;
e) fluorine-containing anions having a stoichiometric equivalent as fluoride that is from 0.05 to 2.0 g/l;
f) 0,5 to 20 g/l nitrate anions; and
g) a dissolved accelerator component other than nitrite consisting of at least one substance selected from the group consisting of:

- 0.3 to 4 g/l of chlorate ions;
- 0.05 to 2 g/l of m-nitrobenzene sulphonate ions;
- 0.05 to 2 g/l of m-nitrobenzoate ions;
- 0.05 to 2 g/l of p-nitrophenol;
- 0.005 to 0.15 g/l of hydrogen peroxide in free or bound form;
- 0.1 to 10 g/l of hydroxylamine in free or bound form; and
- 0.1 to 10 g/l of reducing sugar

15. A process as recited in one or more of claims 1 to 13, wherein the zinc phosphating solution used in step (I) comprises 0.30 to 3.0 g/l of zinc cations and further comprises at least one or more of:

c) 0.1 to 2.0 g/l of nickel(II) cations;
e) fluorine-containing anions having a stoichiometric equivalent as fluoride that is from 0.1 to 2.0 g/l;
f) 1 to 20 g/l nitrate anions;
g) a dissolved accelerator component other than nitrite consisting of at least one substance selected from the group consisting of:

- 0.3 to 4 g/l of chlorate ions;
- 0.05 to 2 g/l of m-nitrobenzene sulphonate ions;
- 0.05 to 2 g/l of m-nitrobenzoate ions;
- 0.05 to 2 g/l of p-nitrophenol;
- 0.005 to 0.15 g/l of hydrogen peroxide in fi-ee or bound form;
- 0.1 to 10 g/l of hydroxylamine in free or bound form; and
- 0.1 to 10 g/l of reducing sugar

16. A process as recited in one or more of claims 1 to 15, wherein the surface-covering crystalline zinc phosphate layer has a coating weight in the range from 2 to 3 g/m^2 on the zinc or zinc alloy, steel, galvanized steel, or alloy-galvanized steel portions.

17. A process as recited in claim 16, wherein the zinc or zinc alloy portion, and the steel, galvanized steel, or alloy-galvanized steel portion have a weight loss of 1.7 g/m^2, and the aluminum or aluminum alloy portion has a weight loss of 0.1 to 0.6 g/m^2.

18. A process as recited in one or more of claims 1 to 17, wherein in step (I) the at least one aluminum or aluminum alloy portion is etched to remove oxides.

Patentansprüche

1. Verfahren zur chemischen Vorbehandlung, vor einer organischen Beschichtung, einer Metallverbundstruktur, die mindestens einen Abschnitt aus Aluminium oder einer Aluminiumlegierung, mindestens einen Abschnitt aus Zink oder einer Zinklegierung und mindestens einen Abschnitt aus Stahl, galvanisiertem Stahl oder legiertem galvanisiertem Stahl enthält, wobei das Verfahren Folgendes umfasst:

(I) Behandeln der Metallverbundstruktur mit einer Zinkphosphatierungslösung, die unter 5 g/l Phosphat-Ionen und über 0,2 g/l Nitrit-Ionen aufweist, wobei die Zinkphosphatierungslösung eine Oberflächen bedeckende kristalline Zinkphosphatschicht mit einem Schichtgewicht im Bereich von 0,5 bis 5 g/m^2 auf den Abschnitten aus Zink oder einer Zinklegierung, Stahl, galvanisiertem Stahl oder legiertem galvanisiertem Stahl bildet, aber ohne eine Zinkphosphatschicht auf dem Abschnitt aus Aluminium oder einer Aluminiumlegierung zu bilden; und
(II) anschließend Inkontaktbringen der Metallverbundstruktur mit einer Behandlungslösung mit einem pH-Wert im Bereich von 3,3 bis 10, welche nicht mehr als 60 % der während Schritt (1) auf den Abschnitten aus Zink oder einer Zinklegierung, Stahl, galvanisiertem Stahl oder legiertem galvanisiertem Stahl gebildeten kristallinen Zinkphosphatschicht auflöst, aber eine Konversionsschicht auf dem Abschnitt aus Aluminium oder einer Aluminiumlegierung bildet,

wobei die in Schritt (1) verwendete Zinkphosphatierungslösung ferner Folgendes umfasst:

a) 0,30 bis 3,0 g/l Zink-Kationen;
b) 0,05 bis 2,0 g/l Mangan(II)-Kationen;

wobei die in Schritt (1) verwendete Zinkphosphatierungslösung einen Wert von -1,0 bis 3,0 Freie-Säure-Punkten sowie eine Konzentration freier Fluorid-Ionen in der Zinkphosphatierungslösung gemäß Verfahrensschritt (1), gemessen in g/l, bei einer spezifischen Temperatur T (in °C) aufweist, die unter einem Wert von 8/T liegt.

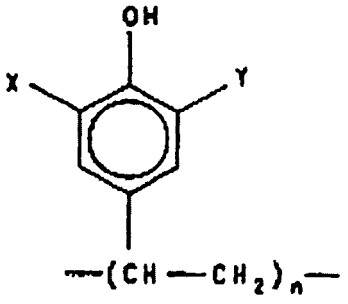
2. Verfahren nach Anspruch 1, wobei die in Schritt (1) verwendete Zinkphosphatierungslösung eine Temperatur im Bereich von 20 °C bis 40 °C aufweist; und in Schritt (11) die Behandlungslösung nicht mehr als 25 %, vorzugsweise nicht mehr als 10 %, der in Schritt (1) abgeschiedenen kristallinen Zinkphosphatschicht auflöst.

3. Verfahren nach Anspruch 1 oder 2, wobei in Schritt (1) die Zinkphosphatierungslösung eine Temperatur im Bereich von 30 °C bis 35 °C aufweist.

4. Verfahren nach einem oder mehreren der Ansprüche 1 bis 3, wobei die in Schritt (11) verwendete Behandlungslösung einen pH-Wert im Bereich von 3,3 bis 5,5 aufweist und 0,3 bis 1,5 g/l von einem von Hexafluortitanat-Ionen, Hexafluorzirconat-Ionen oder beiden umfasst.

5. Verfahren nach einem oder mehreren der Ansprüche 1 bis 4, wobei die in Schritt (11) verwendete Behandlungslösung ferner 0,01 bis 0,1 g/l Kupferlonen umfasst.

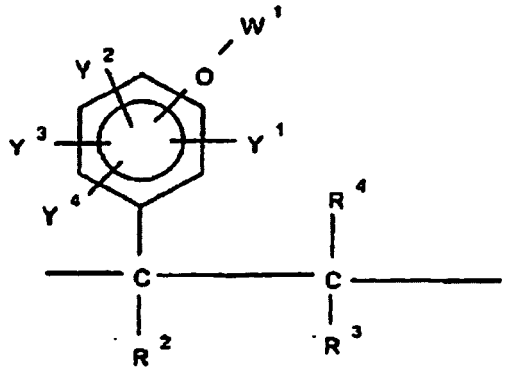
6. Verfahren nach einem oder mehreren der Ansprüche 1 bis 3, wobei die in Schritt (11) verwendete Behandlungslösung einen pH-Wert im Bereich von 3,5 bis 5,8 aufweist und 10 bis 500 mg/l organische Polymere enthält, die aus Poly-4-vinylphenol-Molekülen ausgewählt sind, die der allgemeinen Formel (1) entsprechen:



(I)

wobei n eine ganze Zahl zwischen 5 und 100 ist, jedes von X und Y unabhängig voneinander Wasserstoff oder einen CRR^1OH-Rest bedeutet, wobei jedes von R und R^1 unabhängig voneinander Wasserstoff oder ein aliphatischer oder ein aromatischer Rest mit 1 bis 12 Kohlenstoffatomen ist.

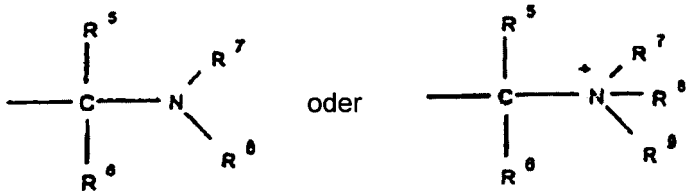
7. Verfahren nach einem oder mehreren der Ansprüche 1 bis 3, wobei die in Schritt (II) verwendete Behandlungslösung einen pH-Wert im Bereich von 3,3 bis 5,8 aufweist und 10 bis 5000 mg/l organische Polymere enthält, von welchen jedes mindestens eine Einheit aufweist, die der allgemeinen Formel (II) entspricht:



(II)

wobei:

- jedes von R^2 bis R^4 unabhängig voneinander und unabhängig von einem Molekül der Komponente zu einem anderen und von einer zu einer anderen Einheit irgendeines dieser Formel entsprechenden Polymermoleküls bei Vorhandensein von mehr als einer solchen Einheit in einem einzelnen Polymermolekül ausgewählt ist aus der Gruppe bestehend aus einem Wasserstoff-Rest, einem Alkyl-Rest mit 1 bis 5 Kohlenstoffatomen und einem Aryl-Rest mit 6 bis 18 Kohlenstoffatomen;
- jedes von Y^1 bis Y^4 unabhängig voneinander und unabhängig von einem Molekül der Komponente zu einem anderen und von einer zu einer anderen Einheit irgendeines dieser Formel entsprechenden Polymermoleküls bei Vorhandensein von mehr als einer solchen Einheit in einem einzelnen Polymermolekül, außer wie weiter unten angegeben, ausgewählt ist aus der Gruppe bestehend aus: einem Wasserstoff-Rest; einem $-CH_2Cl$-Rest; einem Alkyl-Rest mit 1 bis 18 Kohlenstoffatomen; einem Aryl-Rest mit 6 bis 18 Kohlenstoffatomen; einem der allgemeinen Formel $-CR^{12}R^{13}OR^{14}$ entsprechenden Rest, wobei
  jedes von R^{12} bis R^{14} ausgewählt ist aus der Gruppe bestehend aus einem Wasserstoff-Rest, einem Alkyl-Rest, einem Aryl-Rest, einem Hydroxyalkyl-Rest, einem Aminoalkyl-Rest, einem Mercaptoalkyl-Rest und einem Phosphoalkyl-Rest;
  und einem Rest Z, der einer der zwei unmittelbar folgenden allgemeinen Formeln entspricht:



- wobei jedes von R^5 bis R^8 unabhängig voneinander und unabhängig von einem Molekül der Komponente zu einem anderen und von einer zu einer anderen Einheit irgendeines dieser Formel entsprechenden Polymermoleküls bei Vorhandensein von mehr als einer solchen Einheit in einem einzelnen Polymermolekül ausgewählt ist aus der Gruppe bestehend aus einem Wasserstoff-Rest, einem Alkyl-Rest, einem Aryl-Rest, einem Hydroxyalkyl-Rest, einem Aminoalkyl-Rest, einem Mercaptoalkyl-Rest und einem Phosphoalkyl-Rest; und
R^9 ausgewählt ist aus der Gruppe bestehend aus einem Wasserstoff-Rest, einem Alkyl-Rest, einem Aryl-Rest, einem Hydroxy- oder Polyhydroxyalkyl-Rest, einem Amino- oder Polyaminoalkyl-Rest, einem Mercapto- oder Polymercaptoalkyl-Rest, einem Phospho- oder Polyphosphoalkyl-Rest, einem -O-Rest und einem -OH-Rest,
- mindestens eines von Y^1 bis Y^4 in mindestens einer Einheit jedes ausgewählten Polymermoleküls ein wie oben definierter Rest Z ist; und
- W^1 unabhängig von einem Molekül der Komponente zu einem anderen und von einer zu einer anderen Einheit irgendeines dieser Formel entsprechenden Polymermoleküls bei Vorhandensein von mehr als einer solchen Einheit in einem einzelnen Polymermolekül ausgewählt ist aus der Gruppe bestehend aus einem Wasserstoff-Rest, einem Acyl-Rest, einem Acetyl-Rest, einem Benzoyl-Rest; einem 3-Allyloxy-2-hydroxypropyl-Rest; einem 3-Benzyloxy-2-hydroxypropyl-Rest; einem 3-Butoxy-2-hydroxypropyl-Rest; einem 3-Alkyloxy-2-hydroxypropyl-Rest; einem 2-Hydroxyoctyl-Rest; einem 2-Hydroxyalkyl-Rest; einem 2-Hydroxy-2-phenylethyl-Rest; einem 2-Hydroxy-2-alkylphenylethyl-Rest; einem Benzyl, Methyl, Ethyl, Propyl, unsubstituierten Alkyl, unsubstituierten Allyl, unsubstituierten Alkylbenzyl; einem Halogen- oder Polyhalogenalkyl-, oder Halogen- oder Polyhalogenalkenyl-Rest; einem Rest, der abgeleitet ist von einem Kondensationspolymerisationsprodukt von Ethylenoxid, Propylenoxid oder einer Mischung davon durch Entfernen eines Wasserstoffatoms davon; und einem Natrium-, Kalium-, Lithium-, Ammonium- oder substituierten Ammonium-, oder Phosphonium- oder substituierten Phosphonium-Kation-Rest.

8. Verfahren nach Anspruch 7, wobei das organische Polymer, das aus Einheiten gemäß der allgemeinen Formel (II) besteht, ausgewählt ist aus Kondensationsreaktionsprodukten von:

i) Polyvinylphenol;
ii) Formaldehyd; und
iii) mindestens einem sekundären organischen Amin.

9. Verfahren nach Anspruch 8, wobei das organische Polymer, das aus Einheiten gemäß der allgemeinen Formel (II) besteht, Poly(5-vinyl-2-hydroxy-N-benzyl)-N-methylglucamin ist.

10. Verfahren nach einem oder mehreren der Ansprüche 6 bis 9, wobei die in Schritt (II) verwendete Behandlungslösung ferner Hexafluortitanat- und/oder Hexafluorzirconat-Ionen umfasst.

11. Verfahren nach einem oder mehreren der Ansprüche 1 bis 3, wobei die in Schritt (II) verwendete Behandlungslösung einen pH-Wert im Bereich von 3,3 bis 5,8 aufweist und Folgendes enthält:

i) 100 bis 5000 mg/l eines organischen Polymers in Form eines Methylethanolamin-Derivats oder N-Methylglucamin-Derivats von Polyvinylphenol nach Anspruch 9;
ii) 10 bis 2000 mg/l Phosphat-Ionen;
iii) 10 bis 2500 mg/l Hexafluortitanat-Ionen, Hexafluorzirconat-Ionen oder beide; und
iv) 10 bis 1000 mg/l Mangan-Ionen.

12. Verfahren nach einem oder mehreren der Ansprüche 1 bis 3, wobei die in Schritt (II) verwendete Behandlungslösung einen pH-Wert im Bereich von 3,3 bis 4,8 aufweist und 250 bis 1500 mg/l organische Polymere umfasst, die ausgewählt sind aus der Gruppe bestehend aus Homopolymeren und Copolymeren von Acrylsäure, Methacrylsäure

und Estern von Acryl- und Methacrylsäure.

13. Verfahren nach Anspruch 12, wobei die in Schritt (II) verwendete Behandlungslösung ferner Hexafluortitanat-, Hexafluorzirconat- und/oder Hexafluorsilicat-Ionen umfasst.

14. Verfahren nach einem oder mehreren der Ansprüche 1 bis 13, wobei die in Schritt (I) verwendete Zinkphosphatierungslösung 0,30 bis 2,0 g/l Zink-Kationen umfasst und ferner mindestens eines oder mehrere von Folgenden umfasst:

c) 0,1 bis 2,0 g/l Nickel(II)-Kationen;
d) 0,0001 bis 0,03 g/l Kupfer-Kationen;
e) Fluor enthaltende Anionen mit einem stöchiometrischen Äquivalent als Fluorid, das 0,05 bis 2,0 g/l beträgt;
f) 0,5 bis 20 g/l Nitrat-Anionen; und
g) eine aufgelöste Beschleunigerkomponente außer Nitrit, die aus mindestens einer Substanz besteht, die ausgewählt ist aus der Gruppe bestehend aus:

- 0,3 bis 4 g/l Chlorat-Ionen;
- 0,05 bis 2 g/l m-Nitrobenzolsulfonat-Ionen;
- 0,05 bis 2 g/l m-Nitrobenzoat-Ionen;
- 0,05 bis 2 g/l p-Nitrophenol;
- 0,005 bis 0,15 g/l Wasserstoffperoxid in freier oder gebundener Form;
- 0,1 bis 10 g/l Hydroxylamin in freier oder gebundener Form; und
- 0,1 bis 10 g/l reduzierendem Zucker.

15. Verfahren nach einem oder mehreren der Ansprüche 1 bis 13, wobei die in Schritt (I) verwendete Zinkphosphatierungslösung 0,30 bis 3,0 g/l Zink-Kationen umfasst und ferner mindestens eines oder mehrere von Folgenden umfasst:

c) 0,1 bis 2,0 g/l Nickel(II)-Kationen;
e) Fluor enthaltende Anionen mit einem stöchiometrischen Äquivalent als Fluorid, das 0,1 bis 2,0 g/l beträgt;
f) 1 bis 20 g/l Nitrat-Anionen;
g) eine aufgelöste Beschleunigerkomponente außer Nitrit, die aus mindestens einer Substanz besteht, die ausgewählt ist aus der Gruppe bestehend aus:

- 0,3 bis 4 g/l Chlorat-Ionen;
- 0,05 bis 2 g/l m-Nitrobenzolsulfonat-Ionen;
- 0,05 bis 2 g/l m-Nitrobenzoat-Ionen;
- 0,05 bis 2 g/l p-Nitrophenol;
- 0,005 bis 0,15 g/l Wasserstoffperoxid in freier oder gebundener Form;
- 0,1 bis 10 g/l Hydroxylamin in freier oder gebundener Form; und
- 0,1 bis 10 g/l reduzierendem Zucker.

16. Verfahren nach einem oder mehreren der Ansprüche 1 bis 15, wobei die Oberflächen bedeckende kristalline Zinkphosphatschicht ein Schichtgewicht im Bereich von 2 bis 3 g/m^2 auf den Abschnitten aus Zink oder einer Zinklegierung, Stahl, galvanisiertem Stahl oder legiertem galvanisiertem Stahl aufweist.

17. Verfahren nach Anspruch 16, wobei der Abschnitt aus Zink oder einer Zinklegierung und der Abschnitt aus Stahl, galvanisiertem Stahl oder legiertem galvanisiertem Stahl einen Gewichtsverlust von 1,7 g/m^2 aufweisen und der Abschnitt aus Aluminium oder einer Aluminiumlegierung einen Gewichtsverlust von 0,1 bis 0,6 g/m^2 aufweist.

18. Verfahren nach einem oder mehreren der Ansprüche 1 bis 17, wobei in Schritt (I) der mindestens eine Abschnitt aus Aluminium oder einer Aluminiumlegierung geätzt wird, um Oxide zu entfernen.

Revendications

1. Procédé pour un prétraitement chimique, avant l'enduction à l'aide d'un composé organique, d'une structure métallique composite qui contient au moins une portion d'aluminium ou une portion d'alliage d'aluminium, au moins

une portion de zinc ou une portion d'alliage de zinc, et au moins une portion d'acier, une portion d'acier galvanisé ou une portion d'acier galvanisé avec un alliage, le procédé comprenant :

(I) le traitement de la structure métallique composite avec une solution de phosphatage à base de zinc possédant des ions de phosphate en une quantité inférieure à 5 g/l et des ions de nitrite en une quantité supérieure à 0,2 g/l, la solution de phosphatage à base de zinc formant une couche de phosphate de zinc cristalline recouvrant la surface, possédant un poids de la couche dans la plage de 0,5 à 5 g/m^2 sur les portions de zinc ou d'alliage de zinc, d'acier, d'acier galvanisé ou d'acier galvanisé avec un alliage, mais sans former une couche de phosphate de zinc sur la portion d'aluminium ou d'alliage d'aluminium ; et
(II) de manière subséquente, la mise en contact de la structure métallique composite avec une solution de traitement dont le pH se situe dans la plage de 3,3 à 10 qui ne dissout pas la couche de phosphate de zinc cristalline à concurrence de plus de 60 %, que l'on obtient au cours de l'étape (I) sur les portions de zinc ou d'alliage de zinc, d'acier, d'acier galvanisé ou d'acier galvanisé avec un alliage, mais qui produit une couche de conversion sur la portion d'aluminium ou d'alliage d'aluminium,

la solution de phosphatage à base de zinc que l'on utilise à l'étape (I) comprenant en outre :

a) à concurrence de 0,30 à 3,0 g/l, des cations de zinc ;
b) à concurrence de 0,05 à 2,0 g/l, des cations de manganèse(II) ;

la solution de phosphatage à base de zinc que l'on utilise à l'étape (I) possédant une valeur d'acidité libre de -1,0 à 3,0 points, et une concentration d'ions de fluorure libre dans la solution de phosphatage à base de zinc selon l'étape opératoire (I), que l'on mesure en g/l, à une température spécifique T (en °C), qui est inférieure à une valeur de 8/T.

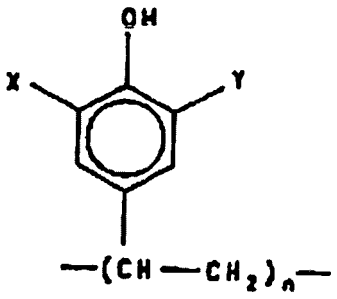
2. Procédé selon la revendication 1, dans lequel la solution de phosphatage à base de zinc que l'on utilise à l'étape (I) possède une température dans la plage de 20 °C à 40 °C ; et à l'étape (II), la solution de traitement déposée à l'étape (I) ne dissout pas de plus de 25 %, de préférence de plus de 10 % la couche de phosphate de zinc cristalline.

3. Procédé selon la revendication 1 ou 2, dans lequel, à l'étape (I), la solution de phosphatage à base de zinc possède une température dans la plage de 30 °C à 35 °C.

4. Procédé selon une ou plusieurs des revendications 1 à 3, dans lequel la solution de traitement que l'on utilise à l'étape (II) possède un pH dans la plage de 3,3 à 5,5 et comprend soit des ions d'hexafluorotitanate, soit des ions d'hexafluorozirconate, ou les deux, à concurrence de 0,3 à 1,5 g/l.

5. Procédé selon une ou plusieurs des revendications 1 à 4, dans lequel la solution de traitement que l'on utilise à l'étape (II) englobe en outre des ions de cuivre à concurrence de 0,01 à 0,1 g/l.

6. Procédé selon une ou plusieurs des revendications 1 à 3, dans lequel la solution de traitement que l'on utilise à l'étape (II) possède un pH dans la plage de 3,5 à 5,8 et contient, à concurrence de 10 à 500 mg/l, des polymères organiques choisis parmi des molécules de poly-4-vinylphénol répondant à la formule générale (I) :

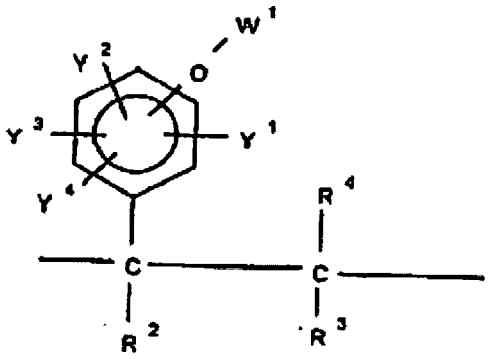


(I)

dans laquelle n est un entier entre 5 et 100, chacun des radicaux X et Y représente, indépendamment l'un de l'autre, un atome d'hydrogène ou une fraction CRR^{1}OH dans laquelle chacun des radicaux R et R^1 représentent, indépen-

damment l'un de l'autre, un atome d'hydrogène ou bien une fraction aliphatique ou aromatique contenant de 1 à 12 atomes de carbone.

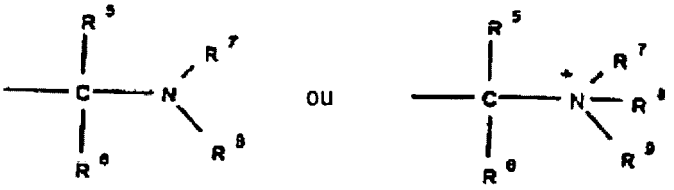
7. Procédé selon une pou plusieurs des revendications 1 à 3, dans lequel la solution de traitement que l'on utilise à l'étape (II) possède un pH dans la plage de 3,3 à 5,8 et contient, à concurrence de 10 à 5000 mg/l, des polymères organiques, chacun possédant au moins une unité répondant à la formule générale (II) :



(II)

dans laquelle :

- chacun des radicaux R^2 à R^4 est choisi, indépendamment l'un de l'autre et indépendamment d'une molécule du composant à l'autre, et indépendamment d'une unité à l'autre de l'une quelconque des molécules polymères répondant à cette formule, lorsqu'il y a plus d'une unité de ce type dans une seule molécule polymère, parmi le groupe constitué par une fraction hydrogène, une fraction alkyle comprenant de 1 à 5 atomes de carbone et une fraction aryle comprenant de 6 à 18 atomes de carbone ;
- chacun des radicaux Y^1 à Y^4 est choisi, indépendamment l'un de l'autre et indépendamment d'une molécule du composant à l'autre, et indépendamment d'une unité à l'autre de l'une quelconque des molécules polymères répondant à cette formule, lorsqu'il y a plus d'une unité de ce type dans une seule molécule polymère, à l'exception de ce qui est indiqué ci-dessous, parmi le groupe constitué par une fraction hydrogène, une fraction $-CH_2Cl$, une fraction alkyle comprenant de 1 à 18 atomes de carbone et une fraction aryle comprenant de 6 à 18 atomes de carbone, une fraction répondant à la formule générale $-CR^{12}R^{13}OR^{14}$, dans laquelle
chacun des radicaux R^{12} à R^{14} est choisi parmi le groupe constitué par une fraction hydrogène, une fraction alkyle, une fraction aryle, une fraction hydroxyalkyle, une fraction aminoalkyle, une fraction mercaptoalkyle et une fraction phosphoalkyle, et
- une fraction Z qui répond à une des deux formules générales indiquées directement ci-après :



- dans lesquelles chacun des radicaux R^5 à R^8 est choisi, indépendamment l'un de l'autre et indépendamment d'une molécule du composant à l'autre, et indépendamment d'une unité à l'autre de l'une quelconque des molécules polymères répondant à cette formule, lorsqu'il y a plus d'une unité de ce type dans une seule molécule polymère, parmi le groupe constitué par une fraction hydrogène, une fraction alkyle, une fraction aryle, une fraction hydroxyalkyle, une fraction aminoalkyle, une fraction mercaptoalkyle et une fraction phosphoalkyle ; et R^9 est choisi parmi le groupe constitué par une fraction hydrogène, une fraction alkyle, une fraction aryle, une fraction hydroxyalkyle ou polyhydroxyalkyle, une fraction aminoalkyle ou polyaminoalkyle, une fraction mercaptoalkyle ou polymercaptoalkyle, une fraction phosphoalkyle ou polyphosphoalkyle, une fraction -O et une fraction -OH ;
- au moins un des radicaux Y^1 à Y^4 dans au moins une unité de chaque molécule polymère sélectionnée représentant une fraction Z telle que mentionnée ci-dessus ; et
- W^1 est choisi, indépendamment d'une molécule du composant à l'autre, et indépendamment d'une unité à

l'autre de l'une quelconque des molécules polymères répondant à cette formule, lorsqu'il y a plus d'une unité de ce type dans une seule molécule polymère, parmi le groupe constitué par une fraction hydrogène, une fraction acyle, une fraction acétyle, une fraction benzoyle, une fraction 3-allyloxy-2-hydroxypropyle, une fraction 3-benzyloxy-2-hydroxypropyle, une fraction 3-butoxy-2-hydroxypropyle, une fraction 3-alcoxy-2-hydroxypropyle, une fraction 2-hydroxyoctyle ; une fraction 2-hydroxyalkyle ; une fraction 2-hydroxy-2-phényléthyle, une fraction 2-hydroxy-2-alkylphényléthyle, une fraction benzyle, une fraction méthyle, une fraction éthyle, une fraction propyle, une fraction alkyle non substituée, une fraction allyle non substituée, une fraction alkylbenzyle non substituée, une fraction halogénoalkyle ou polyhalogénoalkyle ou bien une fraction halogénoalkyle ou polyhalogénoalcényle, une fraction qui dérive d'un produit de polymérisation par condensation d'oxyde d'éthylène, d'oxyde de propylène ou bien d'un de leurs mélanges par suppression d'un de leurs atomes d'hydrogène, et une fraction de cation de sodium, de potassium, de lithium, d'ammonium ou d'ammonium substitué ou bien de phosphonium ou de phosphonium substitué.

8. Procédé selon la revendication 7, dans lequel le polymère organique qui est constitué par des unités répondant à la formule générale (II) est choisi parmi des produits réactionnels de condensation :

i) du polyvinylphénol ;
ii) du formaldéhyde ; et
iii) d'au moins une amine organique secondaire.

9. Procédé selon la revendication 8, dans lequel le polymère organique qui est constitué par des unités répondant à la formule générale (II) est la poly(5-vinyl-2-hydroxy-N-benzyl)-N-méthylglucamine.

10. Procédé selon une ou plusieurs des revendications 6 à 9, dans lequel la solution de traitement que l'on utilise à l'étape (II) comprend en outre des ions d'hexafluorotitanate et/ou des ions d'hexafluorozirconate.

11. Procédé selon une ou plusieurs des revendications 1 à 3, dans lequel la solution de traitement que l'on utilise à l'étape (II) possède un pH dans la plage de 3,3 à 5,8 et contient :

i) à concurrence de 100 à 5000 mg/l, un polymère organique sous la forme d'un dérivé de méthyléthanolamine ou d'un dérivé de N-méthylglucamine de polyvinylphénol selon la revendication 9 ;
ii) à concurrence de 10 à 2000 mg/l, des ions de phosphate ;
iii) à concurrence de 10 à 2500 mg/l, des ions d'hexafluorotitanate, des ions d'hexafluorozirconate, ou les deux ; et
iv) à concurrence de 10 à 1000 mg/l, des ions de manganèse.

12. Procédé selon une ou plusieurs des revendications 1 à 3, dans lequel la solution de traitement que l'on utilise à l'étape (II) possède un pH dans la plage de 3,3 à 4,8 et comprend, à concurrence de 250 à 1500 mg/l, des polymères organiques choisis parmi le groupe constitué par des homopolymères et des copolymères d'acide acrylique, d'acide méthacrylique, et des esters des acides acrylique et méthacrylique.

13. Procédé selon la revendication 12, dans lequel la solution de traitement que l'on utilise à l'étape (II) comprend en outre des ions d'hexafluorotitanate, des ions d'hexafluorozirconate et/ou des ions d'hexafluorosilicate.

14. Procédé selon une ou plusieurs des revendications 1 à 13, dans lequel la solution de phosphatage à base de zinc que l'on utilise à l'étape (I) comprend, à concurrence de 0,30 à 2,0 g/l, des cations de zinc, et comprend en outre au moins un ou plusieurs des éléments ci-après :

c) à concurrence de 0,1 à 2,0 g/l, des cations de nickel(II) ;
d) à concurrence de 0,0001 à 0,03 g/l, des cations de cuivre ;
e) des anions contenant du fluor dont l'équivalent stoechiométrique comme fluor s'élève de 0,05 à 2,0 g/l ;
f) à concurrence de 0,5 à 20 g/l, des anions de nitrate ; et
g) un composant accélérateur à l'état dissout autre qu'un nitrite, constitué par au moins une substance choisie parmi le groupe constitué par :

- à concurrence de 0,3 à 4 g/l, des ions de chlorate ;
- à concurrence de 0,05 à 2 g/l, des ions de m-nitrobenzène sulfonate ;
- à concurrence de 0,05 à 2 g/l, des ions de m-nitrobenzoate ;
- à concurrence de 0,05 à 2 g/l, du p-nitrophénol ;

- à concurrence de 0,005 à 0,15 g/l, du peroxyde d'hydrogène sous forme libre ou sous forme liée ;
- à concurrence de 0,1 à 10 g/l, de l'hydroxylamine sous forme libre ou sous forme liée ; et
- à concurrence de 0,1 à 10 g/litre, un sucre réducteur.

15. Procédé selon une ou plusieurs des revendications 1 à 13, dans lequel la solution de phosphatage à base de zinc que l'on utilise à l'étape (I) comprend, à concurrence de 0,30 à 3,0 g/l, des cations de zinc, et comprend en outre au moins un ou plusieurs des éléments ci-après :

c) à concurrence de 0,1 à 2,0 g/l, des cations de nickel(II) ;
e) des anions contenant du fluor dont l'équivalent stoechiométrique comme fluor s'élève de 0,1 à 2,0 g/l ;
f) à concurrence de 1 à 20 g/l, des anions de nitrate ;
g) un composant accélérateur à l'état dissout autre qu'un nitrite, constitué par au moins une substance choisie parmi le groupe constitué par :

- à concurrence de 0,3 à 4 g/l, des ions de chlorate ;
- à concurrence de 0,05 à 2 g/l, des ions de m-nitrobenzène sulfonate ;
- à concurrence de 0,05 à 2 g/l, des ions de m-nitrobenzoate ;
- à concurrence de 0,05 à 2 g/l, du p-nitrophénol ;
- à concurrence de 0,005 à 0,15 g/l, du peroxyde d'hydrogène sous forme libre ou sous forme liée ;
- à concurrence de 0,1 à 10 g/l, de l'hydroxylamine sous forme libre ou sous forme liée ; et
- à concurrence de 0,1 à 10 g/litre, un sucre réducteur.

16. Procédé selon une ou plusieurs des revendications 1 à 15, dans lequel la couche de phosphate de zinc cristalline recouvrant la surface possède un poids de la couche dans la plage de 2 à 3 g/m^2 sur les portions de zinc ou d'alliage de zinc, d'acier, d'acier galvanisé ou d'acier galvanisé avec un alliage.

17. Procédé selon la revendication 16, dans lequel la portion de zinc ou d'alliage de zinc, et la portion d'acier, d'acier galvanisé ou d'acier galvanisé avec un alliage, possèdent une perte de poids de 1,7 g/m^2, et la portion d'aluminium ou d'alliage d'aluminium possède une perte de poids de 0,1 à 0,6 g/m^2.

18. Procédé selon une ou plusieurs des revendications 1 à 17, dans lequel, à l'étape (I), ladite au moins une portion d'aluminium ou d'alliage d'aluminium est soumise à une attaque à l'acide pour éliminer les oxydes.

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- US 5900073 A **[0010]**
- WO 9912661 A **[0012] [0013] [0014] [0053]**
- DE 19735314 **[0013] [0014]**
- EP 0452638 B1 **[0018]**
- WO 0132953 A **[0026]**
- GB 2199047 A **[0039]**
- US 2089H H **[0051]**
- EP 0319016 B1 **[0056]**
- EP 008942 B1 **[0064]**