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(54) METHOD FOR PROVIDING METAL SURFACES WITH PROTECTION AGAINST CORROSION

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(57) ABSTRACT

A process for the anti-corrosive treatment of vehicle bodies or domestic appliances which have, at least in part, a metal surface and wherein this metal surface consists of at least 90%, based on the metal surface, zinc, aluminum and/or magnesium and/or alloys of these metals with one another or with other alloying elements, wherein the vehicle bodies or domestic appliances are cleaned, passivated and painted, characterised in that, for the purpose of passivation, the vehicle bodies or domestic appliances are contacted with an aqueous solution having a pH of 1 to 12 and containing complex fluorides of Ti, Zr, Hf, Si and/or B in a quantity such that the content of Ti, Zr, Hf, Si and/or B is 20 to 500 mg/l, and 50 to 2000 mg/l organic polymers, the composition of the aqueous solution being selected such that no crystalline zinc-containing phosphate layer is formed on the metal surface.

METHOD FOR PROVIDING METAL SURFACES WITH PROTECTION AGAINST CORROSION

[0001] This invention relates to the field of the anti-corrosive treatment of vehicle bodies or domestic appliances, wherein an anti-corrosive coating is produced on selected non-ferrous surfaces. It is particularly suitable for metal components having surfaces of two or more different non-ferrous metals. A particular feature of the present invention is the fact that no toxic chromium has to be used.

[0002] An extensive prior art exists for the deposition of anti-corrosive coatings on bright metal surfaces to increase corrosion protection. A few examples of documents relating particularly to the chromium-free treatment of aluminum surfaces are listed below. This type of treatment is generally also suitable for zinc surfaces. The term "conversion treatment" used here means that components of the treatment solution react chemically with the metal surface resulting in an anti-corrosive coating in which both components of the treatment solution and metal atoms from the metal surface are incorporated.

[0003] The chromium-free conversion treatment of aluminum surfaces with fluorides of boron, silicon, titanium or zirconium in combination with organic polymers to achieve permanent corrosion protection and to produce a base for subsequent painting is known in principle:

[0004] U.S. Pat. No. 5,129,967 discloses treatment baths for a no-rinse treatment (referred to there as "dried in place conversion coating") of aluminum, containing:

> **[0005]** (a) 10 to 16 g/l polyacrylic acid or homopolymers thereof,
>
> **[0006]** (b) 12 to 19 g/l hexafluorozirconic acid,
>
> **[0007]** (c) 0.17 to 0.3 g/l hydrofluoric acid and
>
> **[0008]** (d) up to 0.6 g/l hexafluorotitanic acid.

[0009] EP-B-8 942 discloses treatment solutions, preferably for aluminum cans, containing:

> **[0010]** (a) 0.5 to 10 g/l polyacrylic acid or an ester thereof and
>
> **[0011]** (b) 0.2 to 8 g/l of at least one of the compounds H_2ZrF_6, H_2TiF_6 and H_2SiF_6, the pH of the solution being less than 3.5,

[0012] and an aqueous concentrate for regenerating the treatment solution, containing:

> **[0013]** (a) 25 to 100 g/l polyacrylic acid or an ester thereof,
>
> **[0014]** (b) 25 to 100 g/l of at least one of the compounds H_2ZrF_6, H_2TiF_6 and H_2SiF_6, and
>
> **[0015]** (c) a source of free fluoride ions providing 17 to 120 g/l free fluoride.,

[0016] DE-C-24 33 704 describes treatment baths to increase paint adhesion and permanent corrosion protection on aluminum, among other materials, which may contain 0.1 to 5 g/l polyacrylic acid or salts or esters thereof and 0.1 to 3.5 g/l ammonium fluorozirconate, calculated as ZrO_2. The pH of these baths may vary over a broad range. The best results are generally obtained when the pH is 6-8.

[0017] U.S. Pat. No. 4,992,116 describes treatment baths for the conversion treatment of aluminum with a pH of between about 2.5 and 5, which contain at least three components:

> **[0018]** (a) phosphate ions in a concentration range of between 1.1×10^{-5} and 5.3×10^{-3} mol/l corresponding to 1 to 500 mg/l,
>
> **[0019]** (b) 1.1×10^{-5} to 1.3×10^{-3} mol/l of a fluoro acid of an element selected from the group consisting of Zr, Ti, Hf and Si (corresponding to 1.6 to 380 mg/l depending on the element) and
>
> **[0020]** (c) 0.26 to 20 g/l of a polyphenol compound, obtainable by reacting poly(vinylphenol) with aldehydes and organic amines.

[0021] A molar ratio of about 2.5:1 to about 1:10 should be maintained between the fluoro acid and the phosphate.

[0022] WO 92/07973 teaches a chromium-free treatment process for aluminum which uses as its main components 0.01 to about 18 wt. % H_2ZrF_6 and 0.01 to about 10 wt. % of a 3-(N-C_1-C_4 alkyl-N-2-hydroxyethylaminomethyl)-4-hydroxystyrene polymer in an acidic aqueous solution. Optional components are 0.05 to 10 wt. % dispersed SiO_2, 0.06 to 0.6 wt. % of a solubility promoter for the polymer and surfactant.

[0023] Vehicle bodies, such as car bodies, are currently assembled from steel and/or other metallic materials, such as galvanised steel or aluminum. After assembly, the bodies are cleaned and subjected to a conversion treatment before painting, to achieve adequate corrosion protection and adequate paint adhesion. The bodies are then painted, generally these days by cathodic electrodeposition coating. Domestic appliances containing metal components, such as refrigerators, freezers, washing machines, tumble driers, cookers, microwave ovens or even metal furniture, may be subjected to a similar process. Owing to the lower corrosion protection requirements for these items, they are generally coated with a powder coating after the conversion treatment.

[0024] Phosphating is widespread as a conversion treatment for domestic appliances. For vehicle bodies, conversion treatment takes place exclusively as so-called "layer-forming" zinc phosphating. For this purpose, the vehicle bodies are contacted with an aqueous solution having a pH of about 2.5 to about 3.8, containing about 0.3 to 2 g/l zinc ions and about 10 to about 20 g/l phosphate ions. These phosphating solutions often also contain about 0.3 to 2 g/l manganese ions and often nickel or copper ions. With this treatment, a layer of crystalline zinc iron phosphates is formed on steel surfaces and a layer of crystalline zinc phosphates on zinc or aluminum surfaces.

[0025] So that these crystalline, zinc-containing phosphate layers develop an adequate effect for corrosion protection and paint adhesion, the actual phosphating step is accompanied by additional steps. For example, before phosphating, the metal surfaces are first cleaned, generally in several steps, and then activated. For the activation step, the metal surfaces are contacted with a solution which mainly contains secondary alkali metal phosphates and suspended colloidal titanium phosphates. This step must be very carefully controlled in order to guarantee sufficient quality of the subsequent phosphating. In particular, compared with phosphating baths, the activating baths are consumed relatively quickly, so that they have to be renewed at short intervals of a few days to several weeks. The monitoring and care of the activation baths therefore represents a considerable proportion of the care and monitoring expenditure for a phosphating line.

[0026] The actual phosphating step is generally followed by so-called post-passivation. As a result of this post-passivation, any pores remaining in the crystalline phosphate layer are closed and corrosion protection and paint adhesion are improved. To this end, the phosphated metal surfaces are contacted with an aqueous solution which may contain various components. At present, post-passivation solutions based on hexavalent chromium, complex fluorides of titanium and/or hafnium, reactive polymers of vinyl phenol derivatives or copper ions are in practical use. These post-passivation baths also have to be checked and adjusted regularly.

[0027] A conversion treatment in the form of phosphating therefore generally requires, in addition to cleaning, at least three treatment baths for activation, phosphating and post-passivation, all of which have to be regularly checked and, if necessary, adjusted or renewed. These at least three baths that are required and the additional rinsing baths between them mean that a large space and high investments are required, thus increasing costs for the manufacture of vehicle bodies and domestic appliances.

[0028] At present, car bodies generally contain surfaces of steel, often in conjunction with surfaces of aluminum and/or galvanised or alloy-galvanised steel. However, car bodies and domestic appliances, apart from plastics parts, may be assembled in such a way that the metal surfaces thereof represent exclusively non-ferrous surfaces. Examples of these non-ferrous surfaces are surfaces of zinc (by the use of galvanised steel), aluminum, magnesium or alloys of these elements with one another or with other metals. Even for the anti-corrosive treatment of items of this type, the phosphating described above is used exclusively at present.

[0029] An object of the present invention is to reduce the cost of anti-corrosive treatment for car bodies or domestic appliances compared with the prior art. The present invention is based on the knowledge that the complex process sequence for phosphating may be made shorter if the metal surfaces of the car bodies or domestic appliances have virtually no iron surfaces.

[0030] The present invention relates to a process for the anti-corrosive treatment of vehicle bodies or domestic appliances which, at least in part, have a metal surface and wherein this metal surface consists of at least 90%, based on the metal surface, zinc, aluminum and/or magnesium and/or alloys of these metals with one another or with other alloying elements, wherein the vehicle bodies or domestic appliances are cleaned, passivated and painted, characterised in that, for the purpose of passivation, the vehicle bodies or domestic appliances are contacted with an aqueous solution having a pH of 1 to 12 and containing complex fluorides of Ti, Zr, Hf, Si and/or B in a quantity such that the content of Ti, Zr, Hf, Si and/or B is 20 to 500 mg/l, and 50 to 2000 mg/l organic polymers, the composition of the aqueous solution being selected such that no crystalline zinc-containing phosphate layer is formed on the metal surface.

[0031] The complex fluorides of the above elements may be introduced into the aqueous solution in the form of the corresponding fluoro acids or the alkali metal and/or ammonium salts thereof. However, it is also possible to form the complex fluorides in the aqueous solution itself by the reaction of hydrofluoric acid or of fluorides with the ions of the above metals. For example, complex fluorides of titanium or zirconium are formed by the reaction of oxides or salts of these elements with hydrofluoric acid.

[0032] In addition to the complex fluorides, the aqueous solution may contain free fluoride, for example in the form of hydrofluoric acid or alkali metal or ammonium fluorides. The content of free fluoride may, for example, be from 0.001 to 1 g/l. This addition of free fluoride increases the pickling action of the aqueous solution and thus the rate of formation of the conversion coating, particularly in the case of hot-dip galvanised steel or aluminum.

[0033] The present process is preferably used for those car bodies and domestic appliances which have no surfaces of uncoated steel. In practice, however, it is not impossible for the steel surface to be bare at cut edges, weld points or grinding points even when coated steel, such as galvanised steel, pre-phosphated steel or organically pre-coated steel, is used. In the context of the present invention, however, a proportion of at least 90%, preferably 95% and particularly preferably 99% of the metal surface should consist of the above-mentioned metals, zinc surfaces generally being surfaces of galvanised steel. Non-metallic surfaces, such as plastics surfaces or surfaces of pre-phosphated or organically pre-coated steel, are not included in this area relation.

[0034] The present process has the great advantage that, compared with conventional phosphating, the activation and post-passivation steps may be omitted. This means that the pre-treatment line is shorter and the time spent on caring for the baths and disposing of them is reduced. This simplifies the process control, reduces the costs and decreases the burden on the environment.

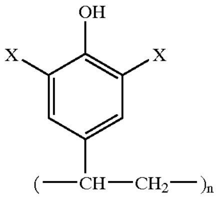
[0035] Aqueous treatment solutions that may be used for the present process are known in principle in the prior art. Examples are mentioned in the introduction. Up to the present, treatment baths of this type have been used for treating less complex components, such as metal strips, metal sheets or metal cans. For complex components, such as car bodies or domestic appliances, these treatment baths have not been used up to now as the sole conversion treatment before painting. In particular, these treatment baths have not been used up to now in processes in which complex metal components were coated by electrodeposition or with a powder coating immediately after the conversion treatment.

[0036] The aqueous solution used for passivation in the process sequence according to the present invention preferably contains the complex fluorides of Ti, Zr, Hf, Si and/or B in a quantity such that the content of Ti, Zr, Hf, Si and/or B is 50 to 400 mg/l. The aqueous solution preferably contains 100 to 1000 mg/l organic polymers.

[0037] The organic polymers may, for example, be selected from epoxy resins, amino resins, tannins, phenol-formaldehyde resins, polycarboxylic acids, polymeric alcohols and/or the esterification products thereof with polycarboxylic acids, poly-4-vinylphenol compounds, amino group-containing homo- or co-polymer compounds and polymers or copolymers of vinyl pyrrolidone. The use of these polymers in the area of metal surface treatment is known.

[0038] The organic polymers may, for example, be selected from poly-4-vinylphenol compounds corresponding to general formula (I):

(I)



[0039] wherein

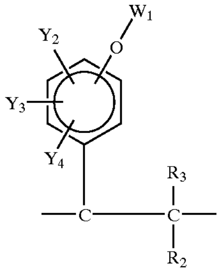
[0040] n represents a number between 5 and 100,

[0041] x independently represents hydrogen and/or CRR_1OH groups wherein R and R_1 represent hydrogen, aliphatic and/or aromatic radicals having 1 to 12 carbon atoms.

[0042] In another embodiment, the organic polymers may be selected from amino group-containing homo- or copolymer compounds, comprising at least one polymer selected from the group consisting of (a), (b), (c) or (d), wherein:

[0043] (a) comprises a polymer material having at least one unit of the formula:

(II')

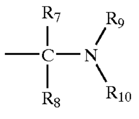


[0044] wherein:

[0045] R_1 to R_3, independently for each of the units, are selected from the group consisting of hydrogen, an alkyl group having 1 to 5 carbon atoms or an aryl group having 6 to 18 carbon atoms;

[0046] Y_1 to Y_4, independently for each of the units, are selected from the group consisting of hydrogen, $—CR_{11}R_5OR_6$, $—CH_2Cl$ or an alkyl or aryl group having 1 to 18 carbon atoms or Z:

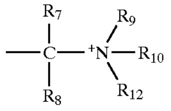
(Z1)



or

-continued

(Z



[0047] but at least a fraction of the Y_1, Y_2, Y_3 or Y_4 of the homo- or co-polymer compound or material must be Z; R_5 to R_{12}, independently for each of the units, are selected from the group consisting of hydrogen, an alkyl, aryl, hydroxyalkyl, aminoalkyl, mercaptoalkyl or phosphoalkyl group;

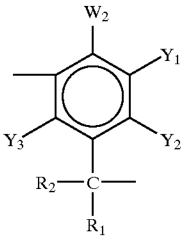
[0048] R_{12} may also be $—O^{(-1)}$ or —OH;

[0049] W_1, independently for each of the units, is selected from the group consisting of hydrogen, an acyl, an acetyl, a benzoyl group; 3-allyloxy-2-hydroxypropyl; 3-benzyloxy-2-hydroxypropyl; 3-butoxy-2-hydroxypropyl; 3-alkyloxy-2-hydroxypropyl; 2-hydroxyoctyl; 2-hydroxyalkyl; 2-hydroxy-2-phenylethyl; 2-hydroxy-2-alkylphenylethyl; benzyl; methyl; ethyl; propyl; alkyl; allyl; alkylbenzyl; haloalkyl; haloalkenyl; 2-chloropropenyl; sodium; potassium; tetraarylammonium; tetraalkylammonium; tetraalkylphosphonium; tetraarylphosphonium or a condensation product of ethylene oxide, propylene oxide or a mixture or a copolymer thereof;

[0050] (b) comprises:

[0051] a polymer material having at least one unit of the formula:

(III)

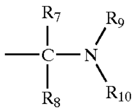


[0052] wherein:

[0053] R_1 to R_2, independently for each of the units, are selected from the group consisting of hydrogen, an alkyl group having 1 to 5 carbon atoms or an aryl group having 6 to 18 carbon atoms;

[0054] Y_1 to Y_3, independently for each of the units, are selected from the group consisting of hydrogen, $—CR_4R_5OR_6$, $—CH_2Cl$ or an alkyl or aryl group having 1 to 18 carbon atoms or Z:

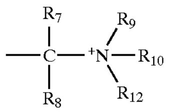
(Z1)



$$-\overset{R_7}{\underset{R_8}{C}}-N\begin{matrix}R_9\\ R_{10}\end{matrix}$$

or

(Z2)



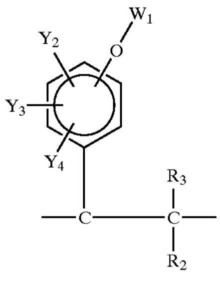
$$-\overset{R_7}{\underset{R_8}{C}}-{}^{+}N\begin{matrix}R_9\\ -R_{10}\\ R_{12}\end{matrix}$$

[0055] but at least a fraction of the Y_1, Y_2, or Y_3 of the end compound must be Z; R_4 to R_{12}, independently for each of the units, are selected from the group consisting of hydrogen, an alkyl, aryl, hydroxyalkyl, aminoalkyl, mercaptoalkyl or phosphoalkyl group; R_{12} may also be $—O^{(-1)}$ or —OH; W_2, independently for each of the units, is selected from the group consisting of hydrogen, an acyl, an acetyl, a benzoyl group; 3-allyloxy-2-hydroxypropyl; 3-benzyloxy-2-hydroxypropyl; 3-alkylbenzyloxy-2-hydroxypropyl; 3-phenoxy-2-hydroxypropyl; 3-alkylphenoxy-2-hydroxypropyl; 3-butoxy-2-hydroxypropyl; 3-alkyloxy-2-hydroxypropyl; 2-hydroxyoctyl; 2-hydroxyalkyl; 2-hydroxy-2-phenylethyl; 2-hydroxy-2-alkylphenylethyl; benzyl; methyl; ethyl; propyl; alkyl; allyl; alkylbenzyl; haloalkyl; haloalkenyl; 2-chloropropenyl or a condensation product of ethylene oxide, propylene oxide or a mixture thereof;

[0056] (c) comprises:

[0057] a copolymer material, wherein at least part of the copolymer has the structure

(II')



[0058] and at least a fraction of the above part is polymerised with one or more monomers which are selected, independently for each unit, from the group consisting of acrylonitrile, methacrylonitrile, methyl acrylate, methyl methacrylate, vinyl acetate, vinyl methyl ketone, isopropenyl methyl ketone, acrylic acid, methacrylic acid, acrylamide, methacrylamide, n-amyl methacrylate, styrene, m-bromostyrene, p-bromostyrene, pyridine, diallyldimethylammonium salts, 1,3-butadiene, n-butyl acrylate, t-butylaminoethyl methacrylate, n-butyl methacrylate, t-butyl methacrylate, n-butyl vinyl ether, t-butyl vinyl ether, m-chlorostyrene, o-chlorostyrene, p-chlorostyrene, n-decyl methacrylate, N,N-diallyl melamine, N,N-di-n-butylacrylamide, di-n-butyl itaconate, di-n-butyl maleate, diethylaminoethyl methacrylate, diethylene glycol monovinyl ether, diethyl fumarate, diethyl itaconate, diethyl vinyl 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, itaconic acid, lauryl methacrylate, methacrylamide, methacrylic acid, methacrylonitrile, N-methylolacrylamide, N-methylolmethacrylamide, N-isobutoxymethylacrylamide, N-isobutoxymethylmethacrylamide, N-alkyloxymethylacrylamide, N-alkyloxymethylmethacrylamide, N-vinyl caprolactam, methyl acrylate, N-methylmethacrylamide, α-methyl styrene, m-methyl styrene, o-methyl styrene, p-methyl styrene, 2-methyl-5-vinylpyridine, n-propyl methacrylate, sodium-p-styrene sulfonate, stearyl methacrylate, styrene, p-styrenesulfonic acid, p-styrenesulfonamide, vinyl bromide, 9-vinylcarbazole, vinyl chloride, vinylidene chloride, 1-vinylnaphthalene, 2-vinylnaphthalene, 2-vinylpyridine, 4-vinylpyridene, 2-vinylpyridine-N-oxide, 4-vinyl pyrimidine, N-vinyl pyrrolidone; and W_1, Y_{1-4} and R_{1-3} are as described under (a);

[0059] (d) comprises a condensation polymer of the polymeric materials (a), (b) or (c), wherein a condensable form of (a), (b), (c) or a mixture thereof is condensed with a second compound which is selected from the group consisting of phenols, tannins, novolak resins, lignin compounds, together with aldehydes, ketones or mixtures thereof, to produce a condensation resin product wherein the condensation resin product, by adding "Z" to at least a part thereof, then reacts further by reaction of the resin product with (1) an aldehyde or ketone (2) a secondary amine to form a final adduct which may react with an acid.

[0060] In a preferred embodiment, the polymer described above is characterised in that at least a fraction of the groups Z of the organic polymer has a polyhydroxyalkylamine functionality, which results from the condensation of an amine or ammonia with a ketose or aldose having 3 to 8 carbon atoms.

[0061] Furthermore, the organic polymer may represent a condensation product of a polyvinylphenol having a molecular weight of 1000 to 10000 with formaldehyde or paraformaldehyde and with a secondary organic amine. This secondary organic amine is preferably selected from methylethanolamine and n-methylglucamine.

[0062] If the organic polymer represents polycarboxylic acid or the anions thereof, it is preferably selected from polymers or copolymers of acrylic acid, methacrylic acid or the esterification products thereof with lower alcohols, for example having 1 to 4 carbon atoms. The solutions or suspensions of these polycarboxylic acids may additionally contain polymeric alcohols, such as polyvinyl alcohol, and/or the esterification products thereof with polymeric alcohol and the polycarboxylic acid may be present together. When the coating is dried, they then cross-link with one another by at least partial ester formation.

[0063] In another embodiment, the aqueous solution may contain polymers or copolymers of vinyl pyrrolidone. Suitable as homo- or co-polymers of vinyl pyrrolidone are, for example, the polymers listed in Table 1 or polymers of the monomers listed there.

TABLE 1

Examples of homo- co-polymers of vinyl pyrrolidone

Description	Trade name and manufacturer
Vinyl pyrrolidone, homopolymer	Luviskol ®, BASF/ISP
Vinyl pyrrolidone/vinyl acetate	Luviskol ®, BASF/ISP
Vinyl pyrrolidone/vinyl caprolactam	Luvitec ®, BASF
Vinyl pyrrolidone/vinylimidazole	Luvitec ®, BASF
Vinyl pyrrolidone/vinylimidazolium methyl sulfate	Luvitec, BASF
Vinyl pyrrolidone/Na methacrylate	Luvitec ®, BASF
Vinyl pyrrolidone/olefin	ISP ®, Antaron
Vinyl pyrrolidone/dimethylaminoethyl methacrylate	ISP ®
Vinyl pyrrolidone/ dimethylaminopropylmethacrylamide	ISP ®, Styleze
Vinyl pyrrolidone/dimethylaminoethyl methacrylate ammonium salt	ISP ®, Gafquat
Vinyl pyrrolidone/vinyl caprolactam/ dimethylaminoethyl methacrylate	ISP ®
Vinyl pyrrolidone/methacrylamidopropyl trimethylammonium chloride	ISP ®, Gafquat
Vinyl pyrrolidone/vinyl caprolactam/ dimethylaminoethyl methacrylate	ISP ®, Advantage
Vinyl pyrrolidone/styrene	ISP ®, Antara

[0064] If polymers or copolymers of vinyl pyrrolidone are used in the process sequence according to the present invention, the application solution preferably has a pH of 1 to 6, narrower ranges possibly being preferred depending on the substrate, the type of application and the time of exposure. For the treatment of aluminum surfaces, a pH of 2 to 4 is preferably selected and for the treatment of zinc or galvanized steel, a pH of 3 to 5.

[0065] The process sequence according to the present invention may also be applied to car bodies or domestic appliances which have some surfaces of pre-phosphated or organically pre-coated steel or correspondingly pre-coated galvanised steel or aluminum. In this case, the pH of the aqueous solution is preferably adjusted to about 3 to about 10. A pH of about 3.5 to about 5 may be preferred. The anti-corrosive coating already present is not attacked by this process and is even partly reinforced in its anti-corrosive effect.

[0066] Depending on the substrate, the aqueous solution may additionally contain 0.001 to 2, preferably 0.005 to 0.5, g/l in each case, of ions of one or more of the metals Mn, Ce, Li, V, W, Mo, Mg, Zn, Co and Ni. For environmental reasons, however, the use of Co and Ni will be avoided if possible. These additional metal ions may further improve the anti-corrosive effect and paint adhesion.

[0067] Furthermore, the aqueous solution may additionally contain 0.001 to 1.5, preferably 0.1 to 1 g/l each of phosphoric acid, phosphorous acid, phosphonic acid and/or the respective anions and/or their respective esters thereof. The esters should be selected such that they are water-soluble or water-dispersible. These additives also improve the anti-corrosive effect and paint adhesion. However, in accordance with the basic concept of the present invention, it should be ensured that a combination of additives leading to the formation of a crystalline, zinc-containing phosphate layer is not selected, as this would lead to a conventional zinc phosphate layer which is known in the prior art and which only brings about an adequate anti-corrosive effect if the activation and post-passivation steps mentioned above are additionally carried out. This, however, is precisely what the present invention is intended to avoid. This may be achieved, for example, if the treatment solution does not simultaneously contain zinc and/or manganese in concentrations of more than 0.3 g/l and phosphoric acid or phosphate ions in concentrations of more than 3 g/l.

[0068] It is advantageous, however, if the aqueous solution also contains one or more components which are known in the technical field of phosphating as so-called phosphating accelerators. These accelerators have the main task, during phosphating, of preventing the formation of bubbles of elemental hydrogen on the metal surface. This effect is also referred to as the depolarisation effect. As with conventional phosphating, this also has the result in the present process that the formation of the conversion coating takes place more rapidly and that it is formed more uniformly. Accordingly, it is preferred for the aqueous solution to contain one or more phosphating accelerators selected from:

[0069] 0.05 to 2 g/l m-nitrobenzene sulfonate ions,

[0070] 0.1 to 10 g/l hydroxylamine in free or bound form,

[0071] 0.05 to 2 g/l m-nitrobenzoate ions,

[0072] 0.05 to 2 g/l p-nitrophenol,

[0073] 1 to 70 mg/l hydrogen peroxide in free or bound form,

[0074] 0.05 to 10 g/l organic N-oxides

[0075] 0.1 to 3 g/l nitroguanidine

[0076] 1 to 500 mg/l nitrite ions

[0077] 0.5 to 5 g/l chlorate ions.

[0078] Since a particular aim of the process sequence according to the present invention is avoiding the use of toxic chromium compounds, it is preferred that the aqueous solution is free from chromium. Although additions of chromium compounds to the aqueous solution could, in individual cases, have a positive effect on the corrosion protection, the corrosion protection that may be achieved using the present process is adequate even without the use of chromium compounds in the area of application in question.

[0079] Car bodies are often made from different materials. For example, steels galvanised in different ways may be combined with one another or with components of aluminum and/or magnesium or the respective alloys thereof. A particular strength of the present process lies in the fact that, even in these cases, effective corrosion protection is created on the different materials during the passivation. Accordingly, a specialised embodiment of the present invention is characterised in that the vehicle bodies or domestic appliances have surfaces of at least two materials selected from zinc, aluminum, magnesium, alloys of these metals with one another or with other alloying elements.

[0080] The aqueous solution used in the passivation step of the process sequence according to the present invention preferably has a temperature between ambient temperature (about 15 to 20° C.) and about 70° C. A temperature of 25 to 40° C. is preferred. The car bodies or domestic appliances may be contacted with the aqueous solution by spraying with the aqueous solution or by dipping in the aqueous solution. Spray processes are preferred. In general, the aqueous solution is left in contact with the car bodies or domestic appliances for a period of about 1 to about 5 minutes for the passivation step. A period of 1 to 3 minutes is preferred in spray processes and a period of 2 to 5 minutes in dip processes.

[0081] According to the present invention, the passivation step is followed by painting the vehicle bodies or domestic appliances with a dipping paint suitable for electrodeposition or with a powder coating. For vehicle bodies, electrodeposition, particularly cathodic electrodeposition, is preferred. Modern, lead-free or low-lead electrodeposition paints capable of being deposited cataphoretically are suitable for this purpose, i.e. dipping paints containing less than 500 mg lead per kg dry solids in the paint suspension. Domestic appliances may also be coated by electrodeposition. However, powder coating is preferred for this application for reasons of cost.

[0082] The process sequence according to the present invention is therefore characterised by the essential steps of cleaning, passivation and painting. Between these essential process steps, one or more rinsing stages with process water, tap water or deionised water may be provided. For the rinsing steps, spray or dip methods may be employed. The examples show a typical process sequence. These are laboratory tests, however, where a longer period of time elapses between passivation and painting than in the industrial manufacture of car bodies or domestic appliances. For this reason, the test sheets were dried after passivation and rinsing by blowing with compressed air and storing in a drying cabinet. In industrial applications, this drying is necessary if painting is to be carried out using a powder coating after passivation. If painting is carried out using electrodeposition, it is not necessary to dry the components after passivation and rinsing before they are introduced into the paint dipping bath.

EXAMPLES

[0083] The following substrates were used for the tests:

[0084] hot-dip galvanised steel sheets (HDG),

[0085] electro-galvanised steel sheets (EG),

[0086] aluminum sheets, Al 6016 grade (AC 120).

[0087] The test sheets were subjected to the following process operation, all steps being carried out by the dipping method:

[0088] 1. Cleaning using an alkaline cleaner: Ridoline^{R} 1250i (2%, 65° C., 5 minutes),

[0089] 2. Rinsing using deionised water,

[0090] 3. Passivation by treatment using a test product according to Table 1 (pH 4, 30° C., 3 minutes),

[0091] 4. Rinsing using deionised water,

[0092] 5. Drying by blowing with compressed air and storage in a drying cabinet at 55° C.,

[0093] 6. Cathodic electrodeposition painting using the lead-free electrodeposition paint Cathoguard^{R} CG 310 from BASF.

[0094] The following corrosion tests were carried out on the sheets pre-treated in this way, the results of which are compiled in Table 2:

[0095] Test under changing climatic conditions according to VDA 621-415, 10 cycles. The creepage at the scribe over half the scribe width (U/2) is entered in Table 2 in mm.

[0096] Flying stones impact test according to VDA 621-427. The paint adhesion is given as the K-value, 1 representing the best value (no paint spalling) and 10 the worst (complete detachment of paint).

[0097] Copper/acetic acid-accelerated salt-spray test according to DIN 50021 (CASS, 10 days) or neutral salt-spray test according to DIN 50021 (SS, 20 days). The creepage is given as in the test under changing climatic conditions.

TABLE 1

Test products

Test product	Composition
Test product 1	75 mg/l Ti as TiF_6^{2-} 125 mg/l condensation product of a polyvinylphenol having a molecular weight of 1000 to 10000 with formaldehyde and n-methylglucamine
Test product 2	75 mg/l Ti as TiF_6^{2-} 250 mg/l vinyl pyrrolidone-vinyl caprolactam copolymer
Test product 3	400 mg/l Zr as ZrF_6^{2-} 750 mg/l modified polyacrylic acid (Acumer^{R} 1510, Rohm and Haas)
Test product 4	400 mg/l Zr as ZrF_6^{2-} 250 mg/l modified vinyl pyrrolidone-vinyl caprolactum copolymer
Test product 5	150 mg/l Ti as TiF_6^{2-} 200 mg/l condensation product of a polyvinylphenol having a molecular weight of 1000 to 10000 with formaldehyde and n-methylglucamine 350 mg/l phosphate 200 mg/l Mn

[0098]

TABLE 2

Corrosion protection results

a) Substrate: aluminum AC120

Test product no.	CASS (DIN 50021) U/2 (mm)	K-value
1	0.5	8
2	0.4	7
cleaned only (comparison)	0.6	9

b) Substrate: EG

Test product no.	SS (DIN 50021) U/2 (mm)	K-value	VDA 621-415 U/2 (mm)	K-value
1	5	9.5	2.5	7
2	5.1	7	1.7	7
3	6.2	9.5		
4	5.1	7		
5			2.8	7
cleaned only (comparison)			2.8	10

Outdoor weathering test (1 year) painted with full system

Test product	U/2	K-value
5	0.2	1.5

c) Substrate: HDG

Test product no.	SS (DIN 50021) U/2 (mm)	K-value	VDA 621-415 U/2 (mm)	K-value
1	4.2	7.5	2.8	8.5
2	3.5	7.5	3.2	8
3	4.8	9.5		
4	3.2	7.5		
5			1.5	8
cleaned only (comparison)			4.8	10

Outdoor weathering test (1 year) painted with full system

Test product	U/2	K-value
5	0.2	2

[0099] Another test was performed to see how the pretreatment process behaves on grinding points on pre-phosphated galvanised steel. In practice, these grinding points occur when defects on a car body are repaired by grinding them off.

[0100] For the test, electro-galvanised, pre-phosphated steel, ground and unground, was treated with test products 1 and 2. The cathodic electrodeposition paint Cathoguard® 310 was then applied. The corrosion test took the form of a test under changing climatic conditions according to VDA 621-415 over 10 cycles, combined with a flying stones impact test according to VDA 621-427. The results are compiled in Table 3.

TABLE 3

Investigations into grinding points. Substrate: electro-galvanised, pre-phosphated steel

	$EG_{prephos}$ unground		$EG_{prephos}$ ground	
Test product	U/2 [mm]	K	U/2 [mm]	K
1	0.3	4	1.0	3.5
2	0.4	3.5	0.9	3

1. A process for the anti-corrosive treatment of vehicle bodies or domestic appliances which have, at least in part, a metal surface and wherein this metal surface consists of at least 90%, based on the metal surface, zinc, aluminum and/or magnesium and/or alloys of these metals with one another or with other alloying elements, wherein the vehicle bodies or domestic appliances are cleaned, passivated and painted,

characterised in that, for the purpose of passivation, the vehicle bodies or domestic appliances are contacted with an aqueous solution having a pH of 1 to 12 and containing complex fluorides of Ti, Zr, Hf, Si and/or B in a quantity such that the content of Ti, Zr, Hf, Si and/or B is 20 to 500 mg/l, and 50 to 2000 mg/l organic polymers, the composition of the aqueous solution being selected such that no crystalline zinc-containing phosphate layer is formed on the metal surface.

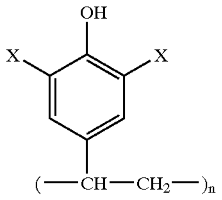
2. A process as claimed in claim 1 wherein the aqueous solution contains complex fluorides of Ti, Zr, Hf, Si and/or B in a quantity such that the content of Ti, Zr, Hf, Si and/or B is 50 to 400 mg/l.

3. A process as claimed in one of claims **1** or **2** wherein the aqueous solution contains 100 to 1000 mg/l organic polymers.

4. A process as claimed in one or more of claims 1 to 3 wherein the organic polymers are selected from epoxy resins, amino resins, tannins, phenol-formaldehyde resins, polycarboxylic acids, polymeric alcohols and/or the esterification products thereof with polycarboxylic acids, poly-4-vinylphenol compounds, amino group-containing homo- or co-polymer compounds and polymers or copolymers of vinyl pyrrolidone.

5. A process as claimed in claim 4 wherein the organic polymers are selected from poly-4-vinylphenol compounds corresponding to general formula (I):

(I)



wherein

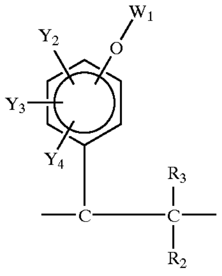
n represents a number between 5 and 100,

x independently represents hydrogen and/or CRR_1OH groups wherein R and R_1 represent hydrogen, aliphatic and/or aromatic radicals having 1 to 12 carbon atoms.

6. A process as claimed in claim 4 wherein the organic polymers are selected from amino group-containing homo- or co-polymer compounds, comprising at least one polymer selected from the group consisting of (a), (b), (c) or (d), wherein:

(a) comprises a polymer material having at least one unit of the formula:

(II)

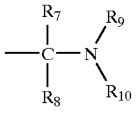


wherein:

R_1 to R_3, independently for each of the units, are selected from the group consisting of hydrogen, an alkyl group having 1 to 5 carbon atoms or an aryl group having 6 to 18 carbon atoms;

Y_1 to Y_4, independently for each of the units, are selected from the group consisting of hydrogen, $—CR_{11}R_5OR_6$, $—CH_2Cl$ or an alkyl or aryl group having 1 to 18 carbon atoms or Z:

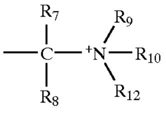
(Z1)



$-\overset{R_7}{\underset{R_8}{C}}-\overset{R_9}{\underset{R_{10}}{N}}$

or

(Z2)



$-\overset{R_7}{\underset{R_8}{C}}-{}^{+}\overset{R_9}{\underset{R_{12}}{N}}-R_{10}$

but at least a fraction of the Y_1, Y_2, Y_3 or Y_4 of the homo- or co-polymer compound or material must be Z; R_5 to R_{12}, independently for each of the units, are selected from the group consisting of hydrogen, an alkyl, aryl, hydroxyalkyl, aminoalkyl, mercaptoalkyl or phosphoalkyl group;

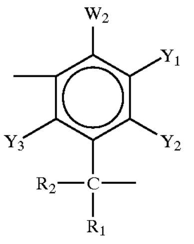
R_{12} may also be $—O^{(-1)}$ or —OH;

W_1, independently for each of the units, is selected from the group consisting of hydrogen, an acyl, an acetyl, a benzoyl group; 3-allyloxy-2-hydroxypropyl; 3-benzyloxy-2-hydroxypropyl; 3-butoxy-2-hydroxypropyl; 3-alkyloxy-2-hydroxypropyl; 2-hydroxyoctyl; 2-hydroxyalkyl; 2-hydroxy-2-phenylethyl; 2-hydroxy-2-alkylphenylethyl; benzyl; methyl; ethyl; propyl; alkyl; allyl; alkylbenzyl; haloalkyl; haloalkenyl; 2-chloropropenyl; sodium; potassium; tetraarylammonium; tetraalkylammonium; tetraalkylphosphonium; tetraarylphosphonium or a condensation product of ethylene oxide, propylene oxide or a mixture or a copolymer thereof;

(b) comprises:

a polymer material with at least one unit of the formula:

(III)

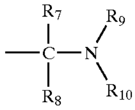


wherein:

R_1 to R_2, independently for each of the units, are selected from the group consisting of hydrogen, an alkyl group having 1 to 5 carbon atoms or an aryl group having 6 to 18 carbon atoms;

Y_1 to Y_3, independently for each of the units, are selected from the group consisting of hydrogen, $—CR_4R_5OR_6$, $—CH_2Cl$ or an alkyl or aryl group having 1 to 18 carbon atoms or Z:

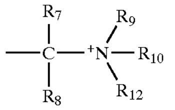
(Z1)



$-\overset{R_7}{\underset{R_8}{C}}-\overset{R_9}{\underset{R_{10}}{N}}$

or

(Z2)



$-\overset{R_7}{\underset{R_8}{C}}-{}^{+}\overset{R_9}{\underset{R_{12}}{N}}-R_{10}$

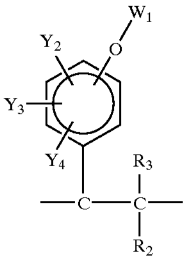
but at least a fraction of the Y_1, Y_2, or Y_3 of the end compound must be Z; R_4 to R_{12}, independently for each of the units, are selected from the group consisting of hydrogen, an alkyl, aryl, hydroxyalkyl, aminoalkyl, mercaptoalkyl or phosphoalkyl group; R_{12} may also be $—O^{(-1)}$ or —OH;

W_2, independently for each of the units, is selected from the group consisting of hydrogen, an acyl, an acetyl, a benzoyl group; 3-allyloxy-2-hydroxypropyl; 3-benzyloxy-2-hydroxypropyl; 3-alkylbenzyloxy-2-hydroxypropyl; 3-phenoxy-2-hydroxypropyl; 3-alkylphenoxy-2-hydroxypropyl; 3-butoxy-2-hydroxypropyl; 3-alkyloxy-2-hydroxypropyl; 2-hydroxyoctyl; 2-hydroxyalkyl; 2-hydroxy-2-phenylethyl; 2-hydroxy-2-alkylphenylethyl; benzyl; methyl; ethyl; propyl; alkyl; allyl; alkylbenzyl; haloalkyl; haloalkenyl; 2-chloropropenyl or a condensation product of ethylene oxide, propylene oxide or a mixture thereof;

(c) comprises:

a copolymer material, wherein at least part of the copolymer has the structure

(II')



and at least a fraction of the above part is polymerised with one or more monomers, which are selected, independently for each unit, from the group consisting of acrylonitrile, methacrylonitrile, methyl acrylate, methyl methacrylate, vinyl acetate, vinyl methyl ketone, isopropenyl methyl ketone, acrylic acid, methacrylic acid, acrylamide, methacrylamide, n-amyl methacrylate, styrene, m-bromostyrene, p-bromostyrene, pyridine, diallyldimethylammonium salts, 1,3-butadiene, n-butyl acrylate, t-butylaminoethyl methacrylate, n-butyl methacrylate, t-butyl methacrylate, n-butyl vinyl ether, t-butyl vinyl ether, m-chlorostyrene, o-chlorostyrene, p-chlorostyrene, n-decyl methacrylate, N,N-diallyl melamine, N,N-di-n-butylacrylamide, di-n-butyl itaconate, di-n-butyl maleate, diethylaminoethyl methacrylate, diethylene glycol monovinyl ether, diethyl fumarate, diethyl itaconate, diethyl vinyl 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, itaconic acid, lauryl methacrylate, methacrylamide, methacrylic acid, methacrylonitrile, N-methylolacrylamide, N-methylolmethacrylamide, N-isobutoxymethylacrylamide, N-isobutoxymethylmethacryl amide, N-alkyloxymethyl acrylamide, N-alkyloxymethylmethacrylamide, N-vinyl caprolactam, methyl acrylate, N-methylmethacrylamide, α-methyl styrene, m-methyl styrene, o-methyl styrene, p-methyl styrene, 2-methyl-5-vinylpyridine, n-propyl methacrylate, sodium-p-styrene sulfonate, stearyl methacrylate, styrene, p-styrenesulfonic acid, p-styrenesulfonamide, vinyl bromide, 9-vinylcarbazole, vinyl chloride, vinylidene chloride, 1-vinylnaphthalene, 2-vinylnaphthalene, 2-vinylpyridine, 4-vinylpyridene, 2-vinylpyridine-N-oxide, 4-vinylpyrimidine, N-vinyl pyrrolidone; and W_1, Y_1-Y_4 and R_1-R_3 are as defined under (a);

(d) comprises a condensation polymer of the polymeric materials (a), (b) or (c), wherein a condensable form of (a), (b), (c) or a mixture thereof is condensed with a second compound which is selected from the group consisting of phenols, tannins, novolak resins, lignin compounds, together with aldehydes, ketones or mixtures thereof, to produce a condensation resin product wherein the condensation resin product, by adding "Z" to at least a part thereof, then reacts further by reaction of the resin product with (1) an aldehyde or ketone (2) a secondary amine to form a final adduct which may react with an acid.

7. A process as claimed in claim 6 wherein at least a fraction of the groups Z of the organic polymer has a polyhydroxyalkylamine functionality, which results from the condensation of an amine or ammonia with a ketose or aldose having 3 to 8 carbon atoms.

8. A process as claimed in claim 6 wherein the organic polymer represents a condensation product of a polyvinylphenol having a molecular weight in the range of 1000 to 10,000 with formaldehyde or paraformaldehyde and with a secondary organic amine.

9. A process as claimed in one or more of claims 1 to 8 wherein the aqueous solution additionally contains 0.001 to 2 g/l in each case of one or more of the metals Mn, Ce, Li, V, W, Mo, Mg, Zn, Co and Ni.

10. A process as claimed in one or more of claims 1 to 9 wherein the aqueous solution additionally contains 0.001 to 1.5 g/l each of phosphoric acid, phosphorous acid, phosphonic acid and/or the respective anions and/or the respective esters thereof.

11. A process as claimed in one or more of claims 1 to 10 wherein the aqueous solution contains one or more phosphating accelerators selected from:

0.05 to 2 g/l m-nitrobenzene sulfonate ions,

0.1 to 10 g/l hydroxylamine in free or bound form,

0.05 to 2 g/l m-nitrobenzoate ions,

0.05 to 2 g/l p-nitrophenol,

1 to 70 mg/l hydrogen peroxide in free or bound form,

0.05 to 10 g/l organic N-oxides

0.1 to 3 g/l nitroguanidine

1 to 500 mg/l nitrite ions

0.5 to 5 g/l chlorate ions.

12. A process as claimed in one or more of claims 1 to 11 wherein the aqueous solution is free from chromium.

13. A process as claimed in one or more of claims 1 to 12 wherein the vehicle bodies or domestic appliances have surfaces of at least two materials selected from zinc, aluminum, magnesium, alloys of these metals with one another or with other alloying elements.

14. A process as claimed in one or more of claims 1 to 13 wherein, after passivation, the vehicle bodies or domestic appliances are coated with a dipping paint suitable for electrodeposition or with a powder coating.

* * * * *