WET ON WET METHOD AND CHROME-FREE ACIDIC SOLUTION FOR THE CORROSION CONTROL TREATMENT OF STEEL SURFACES

Inventors: Stefan Frey, Deidesheim Deutschland (DE); Jens Kromer, Duesseldorf (DE); Silvia Hohagen, Wuppertal (DE); Sophie Cornen, Duesseldorf (DE); Patrick Dronlou, Colombes (FR); Peter Kuhn, Hilden (DE); Franz-Adolf Czika, Neuss (DE)

Correspondence Address:
HENKEL CORPORATION
1001 TROUT BROOK CROSSING
ROCKY HILL, CT 06067 (US)

Assignee: Henkel AG & Co. KGaA, Duesseldorf (DE)

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ABSTRACT
A process for anticorrosion treatment of bare metal surfaces comprising steel surfaces, wherein the bare metal surfaces are contacted with an acidic aqueous solution of a fluoro complex of at least one element M selected from the group B, Si, Ti, Zr and Hf, at least one further component which is selected from among: a buffer system for the pH range from 2.5 to 5.5, nitrate ions, copper ions, silver ions, vanadium or vanadate ions, bismuth ions, magnesium ions, zinc ions, manganese ions, cobalt ions, nickel ions, tin ions, aromatic carboxylic acids with at least two groups containing donor atoms, or derivatives of such carboxylic acids, and silica particles with an average particle size of below 1 µm; and contains no more than 1 mg/l of an organic polymer with allylamine or vinylamine monomers; the metal surfaces are then rinsed with water and thereafter are coated with a cathodically depositeable electro-dipcoating.
WET ON WET METHOD AND CHROME-FREE ACIDIC SOLUTION FOR THE CORROSION CONTROL TREATMENT OF STEEL SURFACES

[0001] This application is a continuation under 35 U.S.C. Sections 365(c) and 120 of International Application No. PCT/EP2006/011696, filed 6 Dec. 2006 and published 14 Jun. 2007 as WO 2007/065645, which claims priority from German Application No. 102005059314.3, filed 12 Sep. 2005, each of which is incorporated herein by reference in its entirety.

[0002] The present invention relates to a novel product for the anticorrosion treatment of metal surfaces. In addition, a process is provided for the anticorrosion treatment of metal, in particular, steel surfaces. The anticorrosion treatment is primarily intended as a pre-treatment for a subsequent cathodic electro-dipcoating.

[0003] Anticorrosion agents that involve an acidic aqueous solution of fluoro complexes have been known for some considerable time. They are increasingly employed as a replacement for chromating processes that due to the toxicological properties of chromium compounds are less and less used. Generally, solutions of fluoro complexes of this type contain additional anticorrosion agents that further improve the corrosion protection and paint adhesion.

[0004] DE-A-19 33 013, for example, describes in one embodiment a treatment solution that is an aqueous solution of ammonium hexafluorozirconate, sodium nitrate, cobalt nitrate and sodium m-nitrobenzenesulfonate and has a pH of 5.2. The solution can be used to treat zinc-, steel- or aluminium surfaces. EP-A-1 571 237 describes a treatment solution and treatment methods for iron-, zinc-, aluminium- and magnesium-containing surfaces. This solution has a pH in the range of 2 to 6 and contains 5 to 5000 ppm zirconium and/or titanium as well as 0.1 to 10 ppm free fluoride. In addition, the solution can further contain components selected from chloride, bromate, nitrate, nitrate, permanganate, vanadate, hydrogen peroxide, tungstate, molybdate or each of the corresponding acids. Organic polymers can also be present. After the treatment with a solution of this type, the metal surfaces can be rinsed with a further passivating solution. EP-A-1 405 933 discloses a composition that contains at least one metal from the group Ti, Zr, Hf and Si as well as a fluoride ion source for the treatment of iron- and/or zinc surfaces, wherein defined conditions concerning the concentration ratios of both components are set. In addition, this solution can contain the same additional active substances as in EP 1 571 237. Metal ions selected from the group Ag, Al, Cu, Fe, Mn, Mg, Ni, Co and Zn can be present as further components. DE-A-100 10 758 discloses a treatment solution containing complex fluorides of Ti, Zr, Hf, Si and/or B as well as organic polymers particularly for zinc, aluminium and/or magnesium surfaces. The solution can also contain one or more of the metals Mn, Cr, Cu, Li, V, W, Mo, Mg, Zn, Co and Ni. Further potential additives are compounds that are known phosphatization accelerators for the phosphatization layer formation. WO 95/14539 describes treatment solutions for metal surfaces, particularly for aluminium, which contain complex fluorides of Ti, Zr, Hf, Si, Ge, Sn or B as well as organic hydroxycarboxylic acids containing at least 2 hydroxyl groups (wherein the hydroxyl groups of the carboxylic acid groups are not counted) per carboxylic acid group. A specific example of such an acid is gluconic acid.

[0005] In all these documents, mention is made—either in general terms in the description or specifically in the embodiments—that the metal surfaces treated with the stated solution are dried prior to their being coated with an additional organic coating, such as for example a varnish. However, especially for the manufacture, pre-treatment and painting of automobile body work, because of the short cycle times and the shortest possible length of the pre-treatment line, it is desired that the pre-treated body work be fed into the dip coating bath without being dried, i.e. while still wet. Accordingly, a drying step, in which the pre-treatment layer can be, for example, chemically modified and/or hardened by dewetting, is not desired. Therefore, during the pre-treatment, an anticorrosion layer has to be produced—without a drying step—and which possesses the required corrosion protection and adhesion to paint, prior to the application of a first organic paint layer.

[0006] A coating process that meets these specifications is described in EP-A-1 433 876. Here, the treatment of steel, zinc and aluminum surfaces for example, is carried out with a solution that contains Zr, Ti and/or Hf as well as fluoride ions and additionally a water-soluble polyvinylamine or polyallylamine resin. In the sole embodiment that describes the painting of a still wet, pre-treated metal surface, an aqueous solution of fluorozirconic acid, polyallylamine, zine nitrate, silica and ascorbic acid is employed. It is predicted here, that the organic polymer is a significant component in regard to the corrosion protection and the adhesion to paint. However, the presence of organic polymers in pre-treatment solutions is frequently undesirable as they can lead to difficulties in the waste water treatment.

[0007] Surfaces of zinc, aluminum and galvanized steel can be pre-treated with very differently formulated aqueous solutions of fluoro complexes, and the previously stated requirements can be satisfied. One drawback of the prior art is that with steel surfaces that have not been pre-treated, the previously stated requirements can only be satisfied up to now with a layer-forming zinc phosphatization. Compared with the standard of the layer-forming zinc phosphatization, a pre-treatment with aqueous solutions of fluoro complexes shows significant disadvantages in regard to corrosion protection and adhesion to paint when the pre-treated surfaces are not dried before painting.

[0008] Applicants have discovered this problem can be solved if the aqueous solution of a fluoro complex contains certain additional components. Consequently, in a first aspect, the present invention relates to a process for the anticorrosion treatment of bright metal surfaces, which are at least in part steel surfaces, wherein the metal surfaces are brought into contact with an acidic aqueous solution of a fluoro complex of at least one element M selected from the group B, Si, Ti, Zr and Hf, are rinsed with water and thereafter coated with a cathodically deposite-able electro-dipcoating, characterized in that

a) the aqueous solution contains no more than 1 mg/l of an organic polymer with allylamine or vinylamine monomers (a first organic polymer),
b) the aqueous solution additionally contains at least one further component which is selected from among: nitrate ions, copper ions, silver ions, vanadium or vanadate ions, bismuth ions, magnesium ions, zinc ions, manganese ions,
cobalt ions, nickel ions, tin ions, buffer systems for the pH range from 2.5 to 5.5, aromatic carboxylic acids with at least two groups containing donor atoms, or derivatives of such carboxylic acids, silica particles with an average particle size of below 1 μm,
c) after having been brought into contact with the aqueous solution of the fluoro complex and before being coated with the cathodically depositable electro-dipcoating, the metal surface is not dried.

[0009] In this context, “steel surfaces” are understood to mean surfaces of steel, which are not top-coated with an additional metal, such as for example zinc or its alloys with nickel or aluminum. “Bright” metal surfaces are understood to mean metal surfaces, which are not yet coated with an anticorrosion coating. Accordingly, the process according to the invention concerns the first or sole treatment step, which produces an anticorrosion layer that in turn can serve as the basis for a subsequent coat of paint. Therefore, it is not a post-treatment of a previously produced anticorrosion layer, such as for example a phosphate layer.

SUMMARY OF THE INVENTION

[0010] It is an object of the invention to provide a process for the anticorrosion treatment of bright metal surfaces, which are at least in part steel surfaces, wherein the metal surfaces are brought into contact with an acidic aqueous solution of a fluoro complex of at least one element M selected from the group B, Si, Ti, Zr and Hf, are rinsed with water and thereafter coated with a cathodically depositable electro-dipcoating, characterized in that
A) the aqueous solution contains no more than 1 mg/l of an organic polymer with allylamine or vinylamine monomers,
B) the aqueous solution contains a buffer system for the pH range from 2.5 to 5.5,
C) the aqueous solution additionally contains at least one further component which is selected from among: nitrate ions, copper ions, silver ions, vanadium or vanadate ions, bismuth ions, magnesium ions, zinc ions, manganese ions, cobalt ions, nickel ions, tin ions, aromatic carboxylic acids with at least two groups containing donor atoms, or derivatives of such carboxylic acids, silica particles with an average particle size of below 1 μm,
D) after having been brought into contact with the aqueous solution of the fluoro complex and before being coated with the cathodically depositable electro-dipcoating, the metal surface is not dried.

[0011] It is also an object of the invention to provide a process for the anticorrosion treatment of bright metal surfaces, which are at least in part steel surfaces, wherein the metal surfaces are brought into contact with an acidic aqueous solution of a fluoro complex of at least one element M selected from the group B, Si, Ti, Zr and Hf, are rinsed with water and thereafter coated with a cathodically depositable electro-dipcoating, wherein
A) the aqueous solution contains no more than 1 mg/l of an organic polymer with allylamine or vinylamine monomers,
B) the aqueous solution additionally contains at least one further component which is selected from among: nitrate ions, copper ions, silver ions, vanadium or vanadate ions, bismuth ions, magnesium ions, zinc ions, manganese ions, cobalt ions, nickel ions, tin ions, aromatic carboxylic acids with at least two groups containing donor atoms, or derivatives of such carboxylic acids, silica particles with an average particle size of below 1 μm,
It is a further object of the invention to provide the aforementioned processes characterized in that the aqueous solution contains 0.1 to 300 mg/l, preferably 1 to 30 mg/l of copper and/or silver ions.

It is a further object of the invention to provide the aforementioned processes characterized in that the aqueous solution contains 0.1 to 1000 mg/l of the stated aromatic carboxylic acid or derivatives thereof.

It is a further object of the invention to provide the aforementioned processes characterized in that the aqueous solution contains 0.1 to 1000 mg/l of silicon in the form of silica particles with an average particle size of below 1 μm.

It is a further object of the invention to provide the aforementioned processes characterized in that the aqueous solution contains a buffer system for the pH range from 2.5 to 5.5.

It is a further object of the invention to provide the aforementioned processes characterized in that, after having been brought into contact with the aqueous solution of a fluoro complex and before being coated with the cathodically depositable electro-deposition coating, the metal is rinsed with an aqueous solution which contains one or more components selected from among compounds or salts of the elements cobalt, nickel, tin, copper, titanium and zirconium and/or among water-soluble or water-dispersible organic polymers.

It is an object of the invention to provide a composition comprising an acidic, chromium-free aqueous solution of a fluoro complex of at least one element M selected from among the group B, Si, Ti, Zr and Hf with a pH value in the range from 2 to 5.5 for the treatment of metal surfaces, characterized in that it additionally contains a) a buffer system for the pH range from 2.5 to 5.5, b) one or more components selected from among: copper, tin ions, bismuth ions, aromatic carboxylic acids with at least two groups containing donor atoms, or derivatives of such carboxylic acids and for aqueous solutions with an organic polymer content of no more than 1 mg/l silicon in the form of silica particles with an average size of below 1 μm.

It is a further object of the invention to provide a composition, characterized in that it contains a quantity of fluoro complex such that the concentration of the element M is in the range from 1 to 5000 mg/l, preferably in the range from 5 to 1000 mg/l and in particular in the range from 10 to 500 mg/l.

It is a further object of the invention to provide a composition characterized in that, in the fluoro complex, the element M is selected from among the group Si, Ti, Zr and Hf and in that the aqueous solution contains on average at least 1, preferably at least 3, in particular at least five fluoride ions per ion of the element M.

It is a further object of the invention to provide a composition characterized in that, in the fluoro complex, there are six fluoride ions per ion of the element M and in that the aqueous solution furthermore also contains 1 to 1000 mg/l of fluoride ions which are not attached to the element M.

It is a further object of the invention to provide a composition characterized in that the aromatic carboxylic acid is selected from among hydroxycarboxylic acids, amidocarboxylic acids, nitrocarboxylic acids and carboxylic acids with at least two carboxyl groups, or derivatives thereof.

It is a further object of the invention to provide a composition characterized in that it contains 0.1 to 1000 mg/l of the stated aromatic carboxylic acid or derivatives thereof.

It is a further object of the invention to provide a composition characterized in that it additionally contains 10 to 500 mg/l nitroguanidine.

It is a further object of the invention to provide a composition characterized in that it additionally contains 1 to 5000 mg/l of nitrate ions.

It is a further object of the invention to provide a composition characterized in that it additionally contains 0.1 to 300 mg/l, preferably 1 to 30 mg/l of copper and/or silver ions.

It is a further object of the invention to provide a composition characterized in that it contains no more than 1 mg/l of organic polymer.

It is a further object of the invention to provide a composition, characterized in that it additionally contains 10 to 1000 mg/l, preferably 50 to 500 mg/l of silicon in the form of silica particles with an average particle size of below 1 μm.

It is an object of the invention to provide an aqueous concentrate which, on dilution with water by a factor of between 10 and 100 and if necessary adjustment of the pH value, gives rise to an aqueous solution as described herein.

It is an object of the invention to provide a process for the anticorrosion treatment of bright metal surfaces, characterized in that the metal surfaces are brought into contact with an aqueous solution as described herein.

It is a further object of the invention to provide a process characterized in that, after having been brought into contact with the aqueous solution of a fluoro complex, the metal surface is rinsed with an aqueous solution which contains one or more components selected from among compounds or salts of the elements cobalt, nickel, tin, copper, titanium and zirconium and/or among water-soluble or water-dispersible organic polymers.

It is a further object of the invention to provide a process characterized in that, after having been brought into contact with the aqueous solution of a fluoro complex, the metal surface is rinsed with an aqueous solution which contains one or more components selected from among compounds or salts of the elements cobalt, nickel, tin, copper, titanium and zirconium and/or among water-soluble or water-dispersible organic polymers.

DETAILED DESCRIPTION

The treatment solution can contain aromatic carboxylic acids, as one of the previously stated components, which have at least two groups containing donor atoms in the molecule. Donor atoms are those atoms that carry free electron pairs, by which they can coordinate to transition metal ions. Typical donor atoms are oxygen, nitrogen and sulfur atoms. The carboxylic group of the aromatic carboxylic acid is therefore itself already a group that contains donor atoms. An aromatic carboxylic acid with at least two carboxylic groups in the molecule, therefore falls under the stated definition. Those aromatic carboxylic acids, which carry, for example at least one hydroxyl group, at least one amino group or at least one nitro group in addition to the carboxylic group, also fall under the definition. Examples of these carboxylic acids are the various positional isomers of benzene dicarboxylic acid, especially phthalic acid, or the various positional isomers of hydroxy-, amino- or nitro-benzoic acid.

In general, such aromatic carboxylic acids are preferred, in which at least two groups containing donor atoms are disposed in such a way that through the donor atoms, 5-, 6- or 7-membered chelate complexes with transition metal ions can be formed. Particularly preferred aromatic carboxylic acids are therefore: phthalic acid, salicylic acid, o-aminobenzoic acid or o-nitrobenzoic acid. Instead of aromatic carboxylic acids containing only a single benzene ring, the corresponding acids with condensed ring systems can be used, for example the acids derived from naphthalene or anthracene.
Derivatives of the stated aromatic carboxylic acids can also be employed. Among these are meant those molecules, in which one or more hydrogen atoms of the basic structure (e.g. hydrogen atoms on the aromatic core, hydrogen atoms of the hydroxyl or amino groups or hydrogen atoms of the carboxyl groups) are replaced by other atoms or groups of atoms.

The aforementioned silica particles with an average particle size of below 1 μm are known under various generic names to the person skilled in the art. They are called, for example, colloidal silica, precipitated silica or pyrogenic silica. The average particle size, which is preferably in the range of about 0.01 μm to about 1 μm, can be determined by light scattering methods or by electron microscopy.

In the process according to the invention, an aqueous solution is added that on toxicological grounds is essentially free of chromium (VI) compounds and preferably contains no chromium compounds of any kind. Traces of chromium compounds, which can arrive in the treatment solution by being leached off of stainless steel containers, are not considered to render the solution “chromium containing”. In this context, treatment solutions containing no more than 1 ppm, particularly no more than 0.1 ppm chromium, are understood as “chromium free”. The treatment solutions to be employed according to the invention do not represent phosphatization solutions, i.e. they do not lead to the formation of an amorphous or crystalline phosphate layer. This is achieved in that the treatment solutions preferably contain no more than 1 g/l inorganic phosphate or phosphoric acid, calculated as P2O5. However, phosphate contents in the range of 10 to 500 mg/l, for example, can be tolerated and can even improve the action of the treatment solution.

The stability of concentrates, from which the aqueous treatment solutions to be used in the process according to the invention can be manufactured by dilution with water, can be improved by adding thickeners and/or dispersants. These thickeners and/or dispersants are then also present in a suitably diluted state in the ready for use aqueous treatment solution. Their presence in the treatment solution can be tolerated, such that a treatment solution of this type can be used in the process according to the invention. Accordingly, the aqueous treatment solution can be wherein it contains no more than 1 mg/l of another organic polymer than such a polymer that does not contain allylamine or vinylamine monomers, and that, at a concentration of no more than 50 g/l, has thickening or dispersing properties. Examples of such polymers are polymers or copolymers of unsaturated carboxylic acids, carbohydrates or proteins.

Desirably, the aqueous treatment solution contains no more than 1 mg/l of an organic polymer containing allylamine or vinylamine monomers, preferably 0 to 1 mg/l. However, other polymers can be present. Among these are the previously stated polymers with thickening and/or dispersing properties. Apart from these, the treatment solution can contain additional polymers with known positive activity in anti-corrosion treatment. Exemplary polymers of this type (including those with thickening and/or dispersing properties) are:

- polymers or copolymers of unsaturated alcohols or the esters or ethers thereof;
- polymers or copolymers of unsaturated carboxylic acids, organophosphonic acids, organophosphinic acids or in each case the salts, esters or amides thereof;
- polyamino acids or proteins or in each case the salts, esters or amides thereof;
- carbohydrates or the esters or ethers thereof;
- polyamines, in which the nitrogen atoms are incorporated into the polymer chain;
- polyethers;
- polyvinylphenols and the substitution products thereof;
- epoxy resins, amino resins, tannins, phenol-formaldehyde resins,
- polymers and copolymers of vinyl pyrrolidine.

In so far as these types of polymer are present, their concentration in the aqueous treatment solution is preferably less than 2000 mg/l. On secondary technical grounds, such as for example the simplification of the waste water treatment, it can be advantageous to largely or completely dispense with the presence of organic polymers in the aqueous treatment solution. Consequently, a preferred embodiment of the present invention is wherein the aqueous solution contains no more than 1 mg/l of organic polymer.

The pH of the acidic treatment solution is preferably in the range 2 to 5.5, particularly 3.5 to 5. The pH is preferably adjusted to the stated acidic range by adding the fluoro complex at least partially in the form of an acid. However, it can also be adjusted by means of another acid, for example nitric acid. According to the invention and according to this first aspect of the invention, no measures are required, and preferably should be even avoided, which would dry the metal surface after it has been contacted with the aqueous solution of the fluoro complex and before being coated with the cathodically depositable electro-dipping coating. An unintentional drying can however occur during a unit shutdown when the treated metal surface, for example an automobile body or a part thereof, is exposed to air between the bath containing the aqueous solution of the fluoro complex and the electro-dipping coating bath. This unintentional drying is harmless, however.

The additional components stated in feature b) are preferably present in the following concentration ranges; nitrate ions: 0.1 to 5000 mg/l, preferably 1 to 3000 mg/l, in particular 10 to 100 mg/l copper-, silver-, cobalt- or nickel ions: each 0.1 to 300 mg/l, preferably 1 to 30 mg/l, vanadium- or vanadate ions: 1 to 2000 mg/l, preferably 5 to 500 mg/l (calculated as vanadium), bismuth-, magnesium-, zinc-, manganese- or tin ions: each 1 to 2000 mg/l, preferably 5 to 500 mg/l, buffer system for the pH range 2.5 to 5.5: in sufficient quantity that the pH of the solution does not change by more than 0.2 units when a 1 N acid or base per liter solution is added, aromatic carboxylic acids containing at least two groups containing donor atoms, or derivatives of such acids: 0.01 to 1000 mg/l, preferably 1 to 500 mg/l, silicon in the form of silica particles with an average particle size of less than 1 μm: 10 to 1000 mg/l, preferably 50 to 500 mg/l.

In the context of the present invention, when an “acid”, specifically a “carboxylic acid” is mentioned, then the free acid and/or its anions are to be understood. The person skilled in the art is aware that independently of whether the acid is added in the form of a free acid or in the form of soluble salts in the given concentration range, an equilibrium is reached between the free acid and the salt form, which depends on the pKₐ of the acid in question and the pH of the aqueous solution. Concentrations are calculated as the free
acid. The same is true, for example, for H₂ZrF₆ or other acids, which are present in the aqueous solution.

[0049] An acetic acid/acetate buffer is particularly suitable as the buffer system for the stated pH range. A further suitable buffer system is based on potassium hydrogen phthalate.

[0050] Preferably the aqueous solution contains a quantity of fluoro complex such that the concentration of the metal M is in the range from 1 to 5000 mg/l, preferably in the range from 5 to 1000 mg/l and in particular in the range from 10 to 500 mg/l. Zirconium and/or titanium is particularly preferred as the metal M.

[0051] It is further preferred that in the fluoro complex the element M is selected from the group Si, Ti, Zr, and Hf, and in that the aqueous solution contains on average at least 1, preferably at least 3, in particular at least five fluoride ions per ion of the element M. Here, the statement “on average” means the calculated atom ratio of fluoride ions to M ions in the aqueous solution. The stability of fluoro complexes of the stated metals M leads to the expectation that if the aqueous solution contains less than six fluoride ions per M ion, then the fluoride ions are almost completely attached to the M ions in the form of fluoro complexes. Therefore, in this case the fluoride is essentially totally present as “complex fluoride”.

[0052] However, the aqueous solution can also contain more fluoride ions than is required for the complete formation of hexafluoro complexes. In this case, one can assume that six fluoride ions are present in the fluoro complex and that the excess fluoride ions are present as so-called “free fluoride”. They can be in the form of, for example HF and/or water-soluble salts thereof. In one embodiment of the present invention, six fluoride ions per ion of the metal M (M selected from Si, Ti, Zr, Hf) are present in the fluoro complex, and the aqueous solution still contains 1 to 1000 mg/l of fluoride ions which are not attached to the metal M, which is desirably zirconium.

[0053] In a particularly preferred embodiment, the aqueous solution contains at least 0.1 mg/l, preferably at least 1 mg/l and particularly at least 10 mg/l of nitrate ions. The upper limit of the nitrate concentration is chosen more from economic than technical grounds, the economic grounds also including the costs of the waste water disposal. The upper limit of the nitrate ion concentration can be chosen, for example 5000 mg/l, preferably 3000 mg/l and particularly 1000 mg/l. The aqueous solution can contain copper ions and/or silver ions as additional components according to feature b. They can be present instead of the nitrate ions or be together with them. In this embodiment, the aqueous solution preferably contains 0.1 to 300 mg/l, particularly 1 to 30 mg/l of copper ions and/or silver ions.

[0054] In a further preferred embodiment, the aqueous solution contains at least one aromatic carboxylic acid, as defined above, or derivatives thereof. Salicylic acid is particularly preferred. The aromatic carboxylic acid can be present together with the nitrate ions and/or the copper ions and/or the silver ions. It is preferably present in a concentration of at least 0.1 mg/l, preferably at least 1 mg/l and particularly at least 10 mg/l. The upper limit of the concentration is again more conditional on economics than on technical concerns. For example, the upper concentration level of the aromatic carboxylic acid can be 1000 mg/l, preferably 500 mg/l and especially 400 mg/l.

[0055] In a further preferred embodiment, the aqueous treatment solution contains a buffer system for the pH range 2.5 to 5.5, as already described.

[0056] Accordingly, preferably employable aqueous treatment solutions contain at least one of the components described above in more detail: nitrate ions, copper ions and/or silver ions, aromatic carboxylic acids, silica particles with an average particle size of below 1 µm and/or a buffer system for the pH range 2.5 to 5.5. Two or more of these components can also be present together. The presence of further components in addition to the preferred stated five can have a favourable effect on anticorrosion and paint adhesion. For example, in addition to one or more of the five previously stated components (nitrate ions, copper ions and/or silver ions, aromatic carboxylic acids, silica particles, buffer system), one or more of the following components can be present: vanadium- or vanadate ions, cobalt ions, nickel ions, manganese ions, tin ions, bismuth ions, magnesium ions and zinc ions. Their preferred concentration ranges have already been given above. In this regard, a treatment solution, which in addition to one of the five stated preferred components (nitrate ions, copper ions and/or silver ions, aromatic carboxylic acids, silica particles, buffer system), contains both zinc ions as well as magnesium ions, is particularly preferred.

[0057] Moreover, the aqueous treatment solution can additionally contain aluminum ions. They can be introduced in the form of soluble salts, for example in the form of the nitrates. In this case, the aqueous treatment solution preferably contains 1 to 1000 mg/l, especially 10 to 500 mg/l of aluminum ions. Aluminum ions can serve as “accelerators” for excess free fluoride ions, as with these they form stable fluoro complexes. Free fluoride ions are produced in the aqueous treatment solution because the metal M, for example zirconium, precipitates out, probably in the form of oxides, onto the treated metal surface. In this way, the fluoride ions that were originally attached to the metal M are released. The increased pickling effect of the aqueous solution caused by free fluoride ions can be reduced by the presence of the aluminum ions owing to the complex formation.

[0058] In addition to the already stated components, the aqueous treatment solution can contain compounds that are employed in layer forming phosphatization as so-called “accelerators”. These accelerators have the property of capturing hydrogen atoms that are produced by the pickling attack of the acids on the metal surface. This reaction, also known as “depolarization”, facilitates the attack of the acidic treatment solution on the metal surface and thereby accelerates the formation of the anticorrosion layer. Accelerators, which are listed in the previously stated document DE-A-19933189, can be employed, for example:

[0059] 0.05 to 2 g/l m-nitrobenzenesulfonate ions,
[0060] 0.1 to 10 g/l hydroxylamine in free or bound form,
[0061] 0.05 to 2 g/l m-nitrobenzoate ions,
[0062] 0.05 to 2 g/l p-nitrophenol,
[0063] 1 to 70 mg/l of hydrogen peroxide in free or bound form,
[0064] 0.05 to 10 g/l organic N-oxides,
[0065] 0.01 to 3 g/l, preferably up to 0.5 g/l nitroguanidine,
[0066] 1 to 500 mg/l of nitrite ions,
[0067] 0.5 to 5 g/l chlorate ions.

[0068] It is known from the previously stated document EP-A-1571237 that after the treatment with the aqueous solution of a fluoro complex, the treated metal surface is then rinsed with an aqueous solution that contains one or more components selected from compounds or salts of the elements cobalt, nickel, tin, copper, titanium and zirconium and/or from water-soluble or water-dispersible organic polymers.
Corrosion protection and paint adhesion are further improved by this final rinse. A final rinse of this type also has a positive effect in the course of the process according to the invention. Accordingly, the present invention also includes a process variant, in which after having been brought into contact with the aqueous solution of a fluoro complex and before being coated with the cathodically depositable electro-discounting, the metal surface is rinsed with an aqueous solution that contains one or more components selected from among compounds or salts of the elements cobalt, nickel, tin, copper, titanium and zirconium and/or from among water-soluble or water-dispersible organic polymers.

[0069] In the context of the experiments which led to the previously described inventive process steps, it was clear that an addition of one or more components selected from among tin ions, bismuth ions, buffer systems for the pH range 2.5 to 5.5, aromatic carboxylic acids or derivatives thereof, generally improved the anticorrosion effect of aqueous solutions of fluoro complexes for surfaces of steel, aluminum, zinc and galvanized steel. This is true independently of whether the surfaces are dried or not between the contact with this solution and a subsequent painting. These types of treatment solution are therefore not only advantageously employable in the context of the previously described inventive process cycle, but also show a positive effect for anticorrosion and paint adhesion of metal surfaces in general.

[0070] Accordingly, a second aspect of the present invention rests on the provision of an acidic, chromium-free aqueous solution of a fluoro complex of at least one element M selected from among the group B, Si, Ti, Zr and Hf with a pH in the range from 2 to 5.5 for the treatment of metal surfaces, wherein it additionally contains one or more components selected from among: tin ions, bismuth ions, buffer system for the pH range from 2.5 to 5.51 aromatic carboxylic acids with at least two groups containing donor atoms, or derivatives of such carboxylic acids.

[0071] The treatment solution can contain aromatic carboxylic acids as one of the previously stated components, which have at least two groups containing donor atoms in the molecule. Donor atoms are those atoms that carry free electron pairs, by which they can coordinate to transition metal ions. Typical donor atoms are oxygen, nitrogen and sulfur atoms. The carboxylic group of the aromatic carboxylic acid is therefore already a group that contains donor atoms. An aromatic carboxylic acid with at least two carboxylic groups in the molecule, therefore falls under the stated definition. Those aromatic carboxylic acids, which carry, for example at least one hydroxyl group, at least one amino group or at least one nitro group in addition to the carboxylic group, also fall under the definition. Examples of these carboxylic acids are the various positional isomers of benzene dicarboxylic acid, especially phthalic acid, or the various positional isomers of hydroxy-, amino- or nitro-benzoic acid.

[0072] In general, such aromatic carboxylic acids are preferred, in which at least two groups containing donor atoms are disposed in such a way that through the donor atoms, 5-6 or 7-membered chelate complexes can be formed with transition metal ions. Particularly preferred aromatic carboxylic acids are therefore: phthalic acid, salicylic acid, o-amino benzoic acid or o-nitro benzoic acid. Instead of aromatic carboxylic acids containing only a single benzene ring, the corresponding acids with condensed ring systems can also be used, for example the acids derived from naphthalene or anthracene.

[0073] Derivatives of the stated carboxylic acids can also be employed. Among these are those molecules, in which one or more hydrogen atoms of the basic structure (e.g. hydrogen atoms on the aromatic core, hydrogen atoms of the hydroxyl or amino groups or hydrogen atoms of the carboxyl groups) are replaced by other atoms or groups of atoms.

[0074] For this second aspect of the present invention, the previously made explanations to the essential or additional faculative components are correspondingly valid:

[0075] An aqueous solution is added, which on toxicological grounds, is essentially free of chromium (VI) compounds and preferably contains no chromium compounds of any kind. Traces of chromium compounds, which can arrive in the treatment solution by being leached out of stainless steel containers, are not considered to render the solution “chromate-containing”. In this context, treatment solutions containing no more than 1 ppm, particularly no more than 0.1 ppm chromium, are understood as “chromium free”. The treatment solutions according to the invention do not represent phosphatization solutions, i.e. they do not lead to the formation of an amorphous or crystalline phosphate layer. This is achieved in that the treatment solutions preferably contain no more than 1 g/l inorganic phosphate or phosphoric acid, calculated as PO4 3-. However, phosphate contents in the range of 10 to 500 mg/l, for example, can be tolerated and can even improve the action of the treatment solution.

[0076] The pH of the acidic treatment solution is preferably in the range 2 to 5.5, particularly 3.5 to 5. The pH is preferably adjusted to the stated acidic range by adding the fluoro complex at least partially in the form of an acid. However, it can also be adjusted by means of another acid, for example nitric acid.

[0077] The one or more essential components are preferably present in the following concentrations:

- tin ions: 1 to 2000 mg/l, preferably 5 to 500 mg/l,
- bismuth ions: 1 to 2000, preferably 5 to 500 mg/l,
- buffer system for the pH range 2.5 to 5.5 in sufficient quantity that the pH of the solution does not change by more than 0.2 units when a 1 N acid or base per liter solution is added,

- aromatic carboxylic acids: 0.1 to 1000, preferably 1 to 500 mg/l.

[0078] In addition, this aqueous solution can contain one or more of the following components:

- nitrate ions: 0.1 to 5000 mg/l, preferably 1 to 1000 mg/l,
- copper-, cobalt-, nickel- and/or silver ions: each 0.1 to 300 mg/l, preferably 1 to 30 mg/l,
- vanadum- or vanadate ions: 1 to 2000, preferably 5 to 500 mg/l (calculated as vanadium),
- magnesium ions: 1 to 2000, preferably 5 to 500 mg/l,
- manganese ions: 1 to 2000 mg/l, preferably 5 to 500 mg/l,
- zinc ions: 1 to 2000, preferably 5 to 500 mg/l.

[0079] In this regard, it can be preferred that the aqueous solution contains both zinc ions as well as magnesium ions in addition to at least one of the stated essential components (tin ions, bismuth ions, buffer system for the pH range 2.5 to 5.5, aromatic carboxylic acids or derivatives thereof). Moreover, the presence of copper ions and/or silver ions is preferred.

[0080] An acetate or acetate buffer is particularly suitable as the buffer system for the stated pH range. A further suitable buffer system is based on potassium hydrogen phthalate.

[0081] Preferably the aqueous solution contains a quantity of fluoro complex such that the concentration of the metal M is in the range from 1 to 5000 mg/l, preferably in the range
from 5 to 1000 mg/l and in particular in the range from 10 to 500 mg/l. Zirconium and/or titanium is particularly preferred as the metal M.

[0082] It is further preferred that in the fluoro complex the element M is selected from the group Si, Ti, Zr and Hf, and in that the aqueous solution contains on average at least 1, preferably at least 5, in particular at least five fluoride ions per ion of the element M. Here, the statement “on average” means the calculated atom ratio of fluoride ions to M ions in the aqueous solution. The stability of fluoro complexes of the stated metals M leads to the expectation that if the aqueous solution contains less than six fluoride ions per M ion then the fluoride ions are almost completely attached to the M ions in the form of fluoro complexes. Therefore, in this case the fluoride is essentially totally present as “complex fluoride”.

[0083] However, the aqueous solution can also contain more fluoride ions than is required for the complete formation of hexafluoro complexes. In this case, one can assume that six fluoride ions per M ion are present in the fluoro complex and that the excess fluoride ions are present as so-called “free fluoride”. They can be in the form of, for example HF and/or water-soluble salts thereof. Is one embodiment of the present invention, six fluoride ions per ion of the metal M (M selected from Si, Ti, Zr, HD) are present in the fluoro complex, and the aqueous solution still contains 1 to 1000 mg/l of fluoride ions which are not attached to the metal “M”, which is desirably zirconium.

[0084] In the context of the second aspect of the present invention, when an “acid”, specifically a “carboxylic acid” is mentioned, then the free acid and/or its anions are to be understood. The person skilled in the art is aware that independently of whether the acid is added in the form of a free acid or in the form of soluble salts in the given concentration range, an equilibrium is reached between the free acid and the salt form, which depends on the $K_a$ of the acid in question and the pH of the aqueous solution. Concentrations are calculated as the free acid. The same is true, for example, for H$_2$ZrF$_6$ or other acids, which are present in the aqueous solution.

[0085] In a further preferred embodiment in the second aspect of the present invention, the aqueous solution contains at least one aromatic carboxylic acid, preferably salicylic acid, or derivatives thereof. This can be present together with the bismuth ions and/or the buffer system. It is preferably present in a concentration of at least 0.1 mg/l, preferably at least 1 mg/l and particularly at least 10 mg/l. The upper limit of the concentration is again more conditional on economics than on technical concerns. For example, the upper concentration level of the aromatic hydroxycarboxylic acid can be selected as 1000 mg/l, preferably 500 mg/l and especially 400 mg/l.

[0086] In a further preferred embodiment in the context of the second aspect of the invention, the aqueous treatment solution contains a buffer system for the pH range 2.5 to 5.5, as already described.

[0087] Moreover, the aqueous treatment solution can additionally contain aluminum ions. They can be introduced in the form of soluble salts, for example in the form of the nitrates. In this case, the aqueous treatment solution preferably contains 1 to 1000 mg/l, especially 10 to 500 mg/l of aluminum ions. Aluminum ions can serve as “complexers” for excess free fluoride ions, as with these they form stable fluoro complexes. Free fluoride ions are produced in the aqueous treatment solution because the metal M, for example zirconium, precipitates out, probably in the form of oxides, onto the treated metal surface. In this way, the fluoride ions that were originally attached to the metal M are released. The increased pickling effect of the aqueous solution caused by free fluoride ions can be reduced by the presence of the aluminum ions owing to the complex formation.

[0088] In addition to the already stated components according to the second aspect of the invention, the aqueous treatment solution can contain compounds that are employed in layer forming phosphatization as so-called “accelerators”. These accelerators have the property of capturing hydrogen atoms that are produced by the pickling attack of the acids on the metal surface. This reaction, also known as “depolarization”, facilitates the attack of the acidic treatment solution on the metal surface and thereby accelerates the formation of the anticorrosion layer. Accelerators can be employed, for example, which are listed in the previously stated document DE-A-19933189:

[0089] 0.05 to 2 g/l m-nitrobenzene sulfonate ions,
[0090] 0.1 to 10 g/l hydroxylamine in free or bound form,
[0091] 0.05 to 2 g/l m-nitrobenzolate ions,
[0092] 0.05 to 2 g/l p-nitrophenol,
[0093] 1 to 70 mg/l of hydrogen peroxide in free or bound form.

[0094] 0.05 to 10 g/l organic N-oxides
[0095] 0.01 to 3 g/l, preferably up to 0.5 g/l nitroguanidine
[0096] 1 to 500 mg/l of nitrite ions
[0097] 0.5 to 5 μ mol chloride ions.

[0098] Moreover, the treatment solution can contain polymers with known positive activity in anticorrosion treatment. Examples of this type of polymers are:

a) polymers or copolymers of unsaturated alcohols or the esters or ethers thereof;
b) polymers or copolymers of unsaturated carboxylic acids, organophosphonic acids, organophosphinic acids or in each case the salts, esters or amides thereof;
c) polyamino acids or proteins or in each case the salts, esters or amides thereof;
d) carbohydrates or the esters (including esters of xanthic acid) or ethers thereof;
e) polymers, in which the nitrogen atoms are incorporated into the polymer chain,
f) polyethers,
g) polyvinylphenols and the substitution products thereof,
h) epoxy resins, amino resins, tannins, phenol-formaldehyde resins,
i) polymers and copolymers of vinyl pyrolidone.

[0099] In so far as these types of polymer are present, their concentration in the aqueous treatment solution is preferably less than 2000 mg/l. On secondary technical grounds, such as for example the simplification of the waste water treatment, it can be advantageous to largely or completely dispense with the presence of organic polymers in the aqueous treatment solution. Consequently, a preferred embodiment of the present invention is wherein the aqueous solution contains no more than 1 mg/l of organic polymer. Under this condition, it is further preferred that the aqueous solution additionally contains 10 to 1000 mg/l, preferably 50 to 500 mg/l of silicon in the form of silica particles with an average particle size of less than 1 μm. The stated silica particles with an average particle size of less than 1 μm are known under various generic names to the person skilled in the art. They are called, for example, colloidal silica, precipitated silica or pyrogenic silica. The average particle size, which is preferably in the
range of about 0.01 μm to about 1 μm, can be determined by light scattering methods or by electron microscopy.

According to the second aspect of the present invention, the treatment solution can be manufactured at the place of use by dissolving the stated components in water and adjusting the pH. However, this procedure is unusual in practice. In practice, instead of this, aqueous concentrates are usually provided to the place of use, diluted with water and the pH optionally adjusted to produce the ready-for-use treatment solution. Accordingly, an aqueous concentrate belongs to the second aspect of the invention, which on dilution with water by a factor of about 10 to about 100, particularly by a factor of about 20 to about 50 and optionally adjusted in pH results in an acidic, chromium-free, aqueous solution of fluoro complexes according to the previous description.

For stabilization, the concentrates can contain polymers with thickening and/or dispersing properties. Examples of such polymers are polymers or copolymers of unsaturated carboxylic acids, carbohydrates or proteins. They can be present in a concentration of up to 50 g/l.

On stability grounds, concentrates of this type are often adjusted such that on dilution with water, the pH is not directly in the required range. In this case, after dilution with water, the pH has to be corrected either downwards or upwards. A downwards adjustment is made by adding an acid, wherein either the acid form of the fluoro complex of the metal M or nitric acid is suitable. An upwards adjustment of pH can be effected with any basic substance, for example with a solution of alkali metal hydroxides or -carbonates, ammonia or organic amines. However, basic compounds or salts, for example metal oxides, -hydroxides or -carbonates, which represent the possible active components in the treatment solution, can also be added to increase the pH. For example, magnesium or zinc oxides, -hydroxides or -carbonates can be used here.

A process for the anticorrosion treatment of bright metal surfaces further belongs to the second aspect of the present invention, wherein the metal surface is contacted with a previously described aqueous solution according to the second aspect of the invention.

Optionally, after contact with the aqueous solution of a fluoro complex, the metal surface is then rinsed with an aqueous solution that contains one or more components selected from the group of the elements cobalt, nickel, tin, copper, titanium and zirconium and/or from water-soluble or water-dispersible organic polymers.

The term “bright” metal surface was explained further above in connection with the first aspect of the present invention. This explanation is also correspondingly valid for the second aspect of the present invention.

Independently of whether the treatment of the metal surface with the aqueous solution of a fluoro complex corresponding to the process cycle according to the first aspect of the invention or with an aqueous solution according to the second aspect of the invention, the following is generally valid for this process step:

The bright metal surface is contacted with the acidic, aqueous solution of a fluoro complex for a period of 0.5 to 10 minutes, preferably for 1 to 5 minutes. This can be carried out by dipping into the treatment solution or by spraying the treatment solution. In this regard, the temperature of the aqueous solution of a fluoro complex is preferably in the range 15 to 60°C, especially in the range of 25 to 50°C. After this contact, rinsing is preferably carried out with water, especially fully deionized water. After this, the previously described final rinse can optionally follow. In this case, another rinse is subsequently made with water.

In the process cycle according to the first aspect of the present invention, the treated metal surfaces are transferred without drying into a bath for the cathodic electrodeposition. One can proceed in exactly the same way for the treatment with a solution of fluoro complexes according to the second aspect of the present invention. However, one can also dry the treated metal surface before coating it with a cathodic electrode-deposition or with another coating, such as for example a powder coating.

The subsequent embodiments demonstrate the technical advantages of the process according to the invention or the novel aqueous treatment solutions according to the invention.

EXAMPLES

Sample sheets of cold rolled steel, as is used in the automotive industry, were used as the substrate in the following experiments. All process steps were carried out as dip processes. Abbreviations: FD water—fully deionized water, RT—room temperature, min—minutes, CED—cathodic electro-deposition.

**TABLE 1**

<table>
<thead>
<tr>
<th>Process step</th>
<th>Bath composition</th>
<th>Bath Temp</th>
<th>pH</th>
<th>Treatment time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cleaning</td>
<td>3% Ridoline @ 1562 + 0.3% Rodol @ 1561, commercially available alkaline cleaners from Henkel Corp.</td>
<td>60°C</td>
<td>Alkaline</td>
<td>5 min.</td>
</tr>
<tr>
<td>Rinse</td>
<td>Tap water</td>
<td>RT</td>
<td></td>
<td>1 min.</td>
</tr>
<tr>
<td>Pre-treatment</td>
<td>FD water</td>
<td>RT</td>
<td></td>
<td>1 min.</td>
</tr>
<tr>
<td>Zr (zirconium is added as</td>
<td>FD water</td>
<td>30°C</td>
<td></td>
<td>3 min.</td>
</tr>
<tr>
<td>H₂ZrF₆</td>
<td></td>
<td>(sec Tables)</td>
<td>RT</td>
<td>See Tables</td>
</tr>
<tr>
<td>CED</td>
<td>Electro-depos. “Cathoused 801” 310 from BASF Corporation</td>
<td>50°C</td>
<td></td>
<td>0.5 min.</td>
</tr>
<tr>
<td>Drying (sec Tables)</td>
<td>Drying cabinet</td>
<td>RT</td>
<td></td>
<td>60 min.</td>
</tr>
</tbody>
</table>

**TABLE 2**

<table>
<thead>
<tr>
<th>Bath composition</th>
<th>Climate change test: corrosion (mm)</th>
<th>Climate change test: stone impact damage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comparative Example 1: 150 mg/l Zr, pH 4</td>
<td>3.4</td>
<td>4.5</td>
</tr>
<tr>
<td>Example 1: 150 mg/l Zr + 50 mg/l salicylic acid, pH 4</td>
<td>1.6</td>
<td>4.0</td>
</tr>
</tbody>
</table>
TABLE 2-continued

<table>
<thead>
<tr>
<th>Bath composition</th>
<th>Climate change test: corrosion (mm)</th>
<th>Climate change test: stone impact damage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example 2: 150 mg/l Zr + 200 mg/l nitric acid, pH 4</td>
<td>1.9</td>
<td>3.5</td>
</tr>
<tr>
<td>Comparative Example 2: 150 mg/l Zr + 200 mg/l citric acid, pH 4</td>
<td>9.3</td>
<td>5.0</td>
</tr>
</tbody>
</table>

Results:

[0112] Examples 1 and 2, according to the invention, prove the favorable effect of an addition of salicylic acid, when the pre-treatment layer is dried (second aspect of the invention). In contrast, an addition of citric acid (Comparative Example 2) has a rather negative result.

[0113] Table 3 recites the bath composition for the pre-treatment in the process cycle according to Table 1 without drying after pre-treatment, and corrosion results. Climate change test was according to VDA 621-415: average corrosion after 35 days in mm.

Table 5

<table>
<thead>
<tr>
<th>Bath composition</th>
<th>Climate change test: corrosion (mm)</th>
<th>Climate change test: stone impact damage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comparative Example 5: 150 mg/l Zr</td>
<td>3.1</td>
<td>4.5</td>
</tr>
<tr>
<td>Example 5: 150 mg/l Zr + 20 mg/l Cu, pH 4</td>
<td>1.3</td>
<td>3.7</td>
</tr>
<tr>
<td>Example 6: 150 mg/l Zr + 20 mg/l Cu + 200 mg/l Si, pH 4</td>
<td>1.1</td>
<td>3.2</td>
</tr>
</tbody>
</table>

Results:

[0118] Example 5 proves that the addition of 20 mg/l of copper (as Cu(NO3)2) to the conversion bath in the “wet on wet” process yields significantly better infiltration values in the climate change test. The further addition of 20 mg/l of silicon in the form of colloidal silica (Example 6) yields a significant improvement in the K-value in the stone impact test. Table 6 recites the bath composition for the pre-treatment in the process cycle according to Table 1 without drying (“wet on wet”), after pre-treatment and corrosion results. Climate change test was according to VDA 621-415: average corrosion after 70 days in mm, and stone impact damage after 70 days, scale from 0.5 to 5 according to DIN 55996-1 (the smaller the better).

Table 6

<table>
<thead>
<tr>
<th>Bath composition</th>
<th>Climate change test: corrosion (mm)</th>
<th>Climate change test: stone impact damage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example 7: 150 mg/l Zr + 50 mg/l Si, pH 4</td>
<td>0.9</td>
<td>3.7</td>
</tr>
<tr>
<td>Example 6: 150 mg/l Zr + 5 mg/l Cu + 50 mg/l Si + 50 mg/l nitroguanidine, pH 4</td>
<td>0.7</td>
<td>2.3</td>
</tr>
</tbody>
</table>

Results:

[0119] Examples 7 and 8 in comparison show that the addition of the accelerator nitroguanidine (50 mg/l) to the conversion bath resulted in a further improvement in the climate change test in regard to the corrosive paint infiltration and also significantly smaller K-values in the stone impact damage test.

What is claimed is:

1. A process for anticorrosion treatment of bright metal surfaces, which are at least in part steel surfaces, comprising:

1) contacting metal surfaces that are not yet coated with an anticorrosion coating, said surfaces comprising at least one steel surface, with an acidic aqueous solution of a fluoro complex of at least one element M selected from the group consisting of B, Si, Ti, Zr and Hf, wherein:
a) the aqueous solution comprises no more than 1 mg/l of an organic polymer with allylamine or vinylamine monomers;
b) the aqueous solution comprises a buffer system for the pH range from 2.5 to 5.5;
c) the aqueous solution comprises at least one component selected from the group consisting of: nitrate ions, copper ions, silver ions, vanadium ions, vanadate ions, bismuth ions, magnesium ions, zinc ions, manganese ions, cobalt ions, nickel ions, tin ions, aromatic carboxylic acids having at least two groups containing donor atoms, derivatives of said carboxylic acids, and silica particles having an average particle size of less than 1 μm;
2) rinsing the metal surfaces after step 1); and
3) coating the metal surfaces with a cathodically depositable electro-dipcoating.

2. The process according to claim 1, wherein the aqueous solution further comprises additional organic polymers that do not contain allylamine or vinylamine monomers, in an amount of less than 2000 mg/l, said polymers having thickening and/or dispersing properties and/or anticorrosion activity.

3. The process according to claim 1, wherein the aqueous solution comprises no more than 1 mg/l of organic polymer.

4. The process according to claim 1, wherein the element M is selected from the group consisting of Si, Ti, Zr and Hf; the aqueous solution contains on average at least 1 fluorine ion per ion of the element M and the fluoro complex is present in an amount such that concentration of the element M is from 1 to 5000 mg/l.

5. The process according to claim 1, wherein the aqueous solution comprises 0.1 to 300 mg/l copper ions and/or silver ions.

6. The process according to claim 1, wherein component c) comprises at least one component selected from the group consisting of hydroxy carboxylic acids, aminocarboxylic acids, nitrocarboxylic acids, carboxylic acids with at least two carboxyl groups, and derivatives of said acids.

7. The process according to claim 1, wherein the aqueous solution comprises 10 to 1000 mg/l of silicon in the form of silica particles with an average particle size of less than 1 μm.

8. The process according to claim 1, wherein after having been brought into contact with the aqueous solution and before being coated with the cathodically depositable electro-dipcoating, the metal surface is not dried.

9. A process for anticorrosion treatment of bright metal surfaces, which are at least in part steel surfaces, comprising:
1) contacting metal surfaces that are not yet coated with an anticorrosion coating, said metal surfaces comprising at least one steel surface, with an acidic aqueous solution of a fluoro complex of at least one element M selected from the group consisting of B, Si, Ti, Zr and Hf; wherein:
   a) the aqueous solution comprises no more than 1 mg/l of organic polymer;
   b) the aqueous solution comprises 10 to 1000 mg/l of silicon in the form of silica particles with an average particle size of less than 1 μm;
   c) the aqueous solution comprises at least one component selected from the group consisting of: nitrate ions, copper ions, silver ions, vanadium ions, vanadate ions, bismuth ions, magnesium ions, zinc ions, manganese ions, cobalt ions, nickel ions, tin ions, a buffer system for the pH range from 2.5 to 5.5, aromatic carboxylic acids having at least two groups containing donor atoms, and derivatives of said carboxylic acids;
2) rinsing the metal surfaces after step 1); and
3) coating the metal surfaces with a cathodically depositable electro-dipcoating.

10. The process according to claim 9, wherein the element M is selected from the group consisting of Si, Ti, Zr and Hf and the aqueous solution contains on average at least 1 fluoro ion per ion of the element M.

11. The process according to claim 9, wherein the aqueous solution comprises 0.1 to 300 mg/l copper ions and/or silver ions.

12. The process according to claim 11, wherein the aqueous solution contains a buffer system for the pH range from 2.5 to 5.5.

13. The process according to claim 9, wherein after having been brought into contact with the aqueous solution and before being coated with the cathodically depositable electro-dipcoating, the metal surface is not dried.

14. An acidic, chromium-free aqueous solution of a fluoro complex of at least one element M selected from the group consisting of B, Si, Ti, Zr and Hf, said aqueous solution having a pH value in the range from 2 to 5.5, and comprising:
   a) a buffer system for the pH range from 2.5 to 5.5,
   b) one or more components selected from: copper ions, silver ions, tin ions, bismuth ions, aromatic carboxylic acids with at least two groups containing donor atoms, and derivatives of said carboxylic acids.

15. The aqueous solution according to claim 14, wherein the aqueous solution further comprises silicon in the form of silica particles with an average particle size of less than 1 μm and has an organic polymer content of no more than 1 mg/l; the fluoro complex being present in a quantity such that the concentration of the element M is in a range from 1 to 5000 mg/l.

16. The aqueous solution according to claim 14, wherein the aqueous solution contains no more than 1 mg/l of organic polymers that contain allylamine or vinylamine monomers.

17. The aqueous solution according to claim 16, wherein the aqueous solution further comprises additional organic polymers that do not contain allylamine or vinylamine monomers, in an amount of less than 2000 mg/l, said polymers having thickening and/or dispersing properties and/or anticorrosion activity.

18. The aqueous solution according to claim 14, wherein the aqueous solution additionally contains 10 to 500 mg/l nitroguanidine or 0.1 to 5000 mg/l of nitrate ions.

19. The process according to claim 14, wherein component b) comprises at least one component selected from the group consisting of hydroxy carboxylic acids, aminocarboxylic acids, nitrocarboxylic acids, carboxylic acids with at least two carboxyl groups, and derivatives of said acids.

20. An acidic, chromium-free aqueous solution of a fluoro complex of at least one element M selected from the group consisting of B, Si, Ti, Zr and Hf, said aqueous solution having a pH value in the range from 2 to 5.5, and comprising:
   a) no more than 1 mg/l of organic polymer;
   b) 10 to 1000 mg/l of silicon in the form of silica particles with an average particle size of less than 1 μm; and
e) one or more components selected from among: copper ions, silver ions, tin ions, bismuth ions, buffer systems for the pH range from 2.5 to 5.5, aromatic carboxylic acids with at least two groups containing donor atoms, and derivatives of said carboxylic acids.
21. The aqueous solution according to claim 20, wherein the aqueous solution contains a quantity of fluoro complex such that the concentration of the element M is in the range from 5 to 1000 mg/l.

22. The aqueous solution according to claim 20, wherein the aqueous solution additionally contains 10 to 500 mg/l nitroguanidine or 0.1 to 5000 mg/l of nitrate ions.

23. The aqueous solution according to claim 20, wherein the aqueous solution comprises from 0.1 to 300 mg/l of copper and/or silver ions and 50 to 500 mg/l of silicon in the form of silica particles with an average particle size of below 1 μm.

24. The aqueous solution according to claim 20, wherein the aqueous solution contains on average at least 1 fluorine ion per ion of the element M and, in the fluoro complex, the element M is selected from the group consisting of Si, Ti, Zr and Hf.

25. The aqueous solution according to claim 20, wherein, in the fluoro complex, there are six fluorine ions per ion of the element M and the aqueous solution also contains 1 to 1000 mg/l of fluoride ions which are not attached to the element M.

26. An aqueous concentrate which, on dilution with water by a factor of between 10 and 100, and optional adjustment of pH, gives rise to an aqueous solution according to claim 20.

27. A process for the anticorrosion treatment of bright metal surfaces, wherein the metal surfaces are brought into contact with an aqueous solution according to claim 20.

* * * * *