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

(11) EP 1 863 952 B1

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
06.03.2013 Bulletin 2013/10

(21) Application number: **05851727.7**

(22) Date of filing: **14.11.2005**

(51) Int Cl.:
C23C 22/34 $^{(2006.01)}$ ***C23C 22/83*** $^{(2006.01)}$

(86) International application number:
PCT/US2005/041587

(87) International publication number:
WO 2006/088521 (24.08.2006 Gazette 2006/34)

(54) COMPOSITION AND PROCESS FOR PREPARING PROTECTIVE COATINGS ON METAL SUBSTRATES

ZUSAMMENSETZUNG UND VERFAHREN ZUR HERSTELLUNG VON SCHUTZÜBERZÜGEN AUF METALLSUBSTRATEN

COMPOSITION ET PROCEDE DE PREPARATION DE REVETEMENTS DE PROTECTION SUR DES SUBSTRATS METALLIQUES

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

(30) Priority:
15.02.2005 US 58715
15.02.2005 US 76106
21.04.2005 US 116165
21.04.2005 US 116166

(43) Date of publication of application:
12.12.2007 Bulletin 2007/50

(73) Proprietor: **The United States of America as represented by**
The Secretary of The Navy
Patuxent River, MD 20670-1550 (US)

(72) Inventors:
- **MATZDORF, Craig, A.**
  California, Maryland 20619 (US)
- **NICKERSON, William, C., Jr.**
  Patuxent River, Maryland 20670 (US)

(74) Representative: **Winter, Brandl, Fürniss, Hübner, Röss, Kaiser, Polte - Partnerschaft et al**
Alois-Steinecker-Strasse 22
85354 Freising (DE)

(56) References cited:

WO-A-03/040431	**WO-A-03/040437**
US-A- 4 578 122	**US-A- 5 064 751**
US-A- 5 091 023	**US-A1- 2004 054 044**
US-A1- 2004 104 377	**US-B1- 6 669 764**

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

Printed by Jouve, 75001 PARIS (FR)

Description

ORIGIN OF INVENTION

[0001] The invention described herein was made by employee(s) of the United States Government and may be manufactured and used by or for the Government for governmental purposes without the payment of any royalties thereon or therefor.

BACKGROUND OF THE INVENTION

FIELD OF THE Invention

[0002] This invention relates to compositions and to a process for using said compositions for preparing protective coatings on various metal substrates. The process comprises treating the metal substrates with effective amounts of an acidic aqueous solution containing at least one trivalent chromium compound, at least one fluorozirconate, at least one carboxylic compound and/or polyhydroxy compound, at least one corrosion inhibitor, and optionally effective amounts of fluorometallic compounds such as fluorotitanates, fluorotantalates, fluoroborates, fluorosilicates, divalent zinc compounds, surfactants, wetting agents and/or thickeners. More specifically, this invention relates to stable acidic aqueous solutions and the process for treating various metal substrates including pre-coated metal substrates such as anodized aluminum to improve the metal substrates adhesion bonding and corrosion-resistant properties. The process comprises treating the metal substrates with a stable acidic aqueous solution containing effective amounts of at least one water-soluble trivalent chromium salt, at least one water soluble hexafluorozirconate, at least one water soluble poly or mono-carboxylic compound and/or polyhydroxy compound, and at least one water soluble anti-pitting or corrosion inhibitor. In addition, compounds that can be added to improve the color and stability of the acidic solutions in small but effective amounts include at least one water soluble hexa or tetra-fluorometallic compounds, divalent zinc salts, and effective amounts of water soluble thickeners and/or water soluble surfactants.

[0003] This invention comprises a range of aqueous solutions or compositions of specific chemicals and to the processes for depositing coatings derived from these chemicals onto a variety of metallic substrates including pre-existing metal coated substrates. For example, the compositions or solutions are particularly useful for coating aluminum and aluminum alloy i.e. aluminum conversion coatings to enhance corrosion protection and paint adhesion; for sealing anodic coatings to enhance corrosion protection; for treatment of titanium or titanium alloys for enhanced paint adhesion; for treatment of magnesium alloys for enhanced paint adhesion and corrosion protection; for coating steel for enhanced paint adhesion and rust inhibition; and for post-treatment of phosphate coatings, zinc, zinc-nickel, tin-zinc, and cadmium sacrificial coatings on iron alloys and other metal substrates e.g. steel for enhanced paint adhesion and corrosion protection.

[0004] Many of the current pretreatment, post-treatment and sealer solutions are based on the use of hexavalent chromium chemistry. Hexavalent chromium is highly toxic and a known carcinogen. As a result, the solutions used to deposit these coatings and the coatings per se are toxic. The hexavalent chromium films or coatings do, however, yield outstanding paint adhesion, good corrosion resistance, low electrical resistance and can be easily applied by immersion, spray or wipe-on techniques. However, the environmental laws, executive orders, and local occupational, safety, and health (OSH) regulations are driving the military and the commercial users in search for alternatives. Moreover, the use of hexavalent chromium coatings is becoming more expensive as regulations tighten and costs become prohibitive with future PEL restrictions imposed by the EPA and OSHA. In addition, certain processes like spraying chromate solutions are forbidden at some facilities due to OSH risk, forcing the use of less than optimum alternative solutions. In summary, hexavalent chromate coatings are technically outstanding, but from a life-cycle cost, environmental, and OSH perspective, alternatives are highly desirable. Accordingly, research is underway to develop alternative processes for metal finishing that are technically equivalent or superior to hexavalent chromate coatings without the environmental and health drawbacks.

[0005] In WO 03/040431 A2, WO 03/040437 A1 and US 6 669 764 B1 are disclosed processes for coating metal substrates to improve corrosion protection and adhesion bonding strength using compositions comprising water-soluble trivalent chromium salts, alkali metal hexafluorozirconat, divalent zinc compounds, surfactants and thickeners.

[0006] US 2004/054044 A1 describes the use of benzotriazole as a corrosion inhibitor in an aqueous composition to be coated on metallic surfaces.

[0007] US 4 578 122 discloses a composition containing trivalent chromium for treating metal surfaces to impart a chromium passivate film, wherein carboxylic acids or their salts are used to impart increased clarity and initial hardness to the gelatinous chromate film deposited.

[0008] Many of these alternatives, regardless of composition and methods of application, have a tendency to precipitate solid material from solution especially after heavy usage. This precipitation can, over time, weaken the effectiveness of the coating solution as the active compounds precipitate as insoluble solids. Additionally, the solid precipitations have the potential to clog filters, lines, and pumps for both the immersion and spray applications. Therefore, better compositions are needed to stabilize the acidic solutions for storage and process applications that will not interfere with the deposition process or the subsequent performance of the deposited coating.

SUMMARY OF THE INVENTION

[0009] This invention relates to compositions as defined in claim 12 and processes for preparing corrosion-resistant coatings on various metallic substrates including pre-coated metal substrates such as phosphate coatings or anodized coatings as defined in claim 1. This invention can be utilized to improve the adhesion of various other coatings such as paint to the metal surface and to prevent pitting and corrosion of the metal surface such as aluminum, steel, galvanized surfaces and the like. More specifically, the acidic solutions of this invention also contains effective amounts of at least one water-soluble, corrosion-inhibiting or anti-pitting compound together with stabilizing agents consisting of polyhydroxy compounds and/or water-soluble carboxylic compounds containing one or more carboxylic functional groups having the general formula R-COO- wherein R is hydrogen or a lower molecular weight organic radical or functional group. The solution stabilizers i.e. the carboxylic compounds can be used in the form of their acids or salts. In some cases the salts of the carboxylic stabilizers perform better than their acids. For example, organic acids such as formic, acetic, glycolic, propionic, citric and other short-chain or low molecular weight carboxylic acids that naturally buffer in the mildly acidic pH range can be utilized as the solution stabilizers. The advantage of adding the polyhydroxy or carboxylic stabilizers to the acidic solution is the improved shelf-life and working stability of the solutions. The acidic solutions with the addition of the stabilizing agents had substantially no precipitation after more than twenty-four months of shelf-life evaluation and without any degradation of the as-deposited coating performance.

[0010] Fig's 1-6 show the improved performance of an aluminum alloy coated with the triazole-containing solutions of this invention in comparison to the same coatings without the corrosion-inhibiting triazoles.

[0011] It is therefore an object of this invention to provide a stable acidic aqueous solution comprising trivalent chromium compounds, fluorozirconates, polyhydroxy compounds or carboxylic compounds and an effective amount of an inhibitor for coating metal substrates including pre-coated substrates to improve the adhesion and corrosion-resistance properties of the metal.

[0012] It is another object of this invention to provide a stable acidic aqueous solution having a pH ranging from about 1.0 to 5.5 comprising trivalent chromium compounds, fluorozirconates, anti-pitting compounds and at least one polyhydroxy compound and/or carboxylic compound for treating metal substrates with or without a pre-existing metal coating.

[0013] It is another object of this invention to provide a process for treating metal substrates to provide coatings with an identifiable color, good adhesion and improved corrosion resistance.

[0014] It is a further object of this invention to provide a stable acidic aqueous solution having a pH ranging from about 2.5 to 4.5 comprising trivalent chromium compounds, hexafluorozirconates, corrosion inhibitors and at least one carboxylic or polyhydroxy compound for treating metal substrates at ambient temperatures and higher wherein said acidic solutions contain substantially no hexavalent chromium.

[0015] These and other object of the invention will become apparent by reference to the detailed description when considered in conjunction with the accompanying FIG's. 1 to 6, (photos).

DESCRIPTION OF THE DRAWINGS

[0016]

Fig. 1 (photo) shows the corrosion performance of the aluminum alloy (2024-T3) panel with a conversion coating derived from the composition of Example 1 without the triazole inhibitor.

Fig. 2 (photo) shows the corrosion performance of the aluminum alloy (2024-T3) panel with a conversion coating derived from the composition of Example 1 with the benzotriazole inhibitor.

Fig. 3 (photo) shows the corrosion performance of the aluminum alloy (2024-T3) panel with a conversion coating derived from the composition of Example 2 without the triazole inhibitor.

Fig. 4 (photo) shows the corrosion performance of the aluminum alloy (2024-T3) panel with a conversion coating derived from the composition of Example 2 with the benzotriazole inhibitor.

Fig. 5 (photo) shows the corrosion performance of the aluminum alloy (2024-T3) panel with a conversion coating derived from the composition of Example 3 without the triazole inhibitor.

Fig 6 (photo) shows the corrosion performance of the aluminum alloy (2024-T3) panel with a coating derived from the composition of Example 3 with the benzotriazole inhibitor.

DETAILED DESCRIPTION OF THE INVENTION

[0017] This invention relates to stable acidic aqueous solutions and to the process of using said aqueous solutions having a pH ranging from about 1.0 to 5.5, and preferably from about 2.5 to 4.5 or 3.4 to 4.0 for preparing zirconium-chromium coatings e.g. a conversion coating on metal substrates including, for example, pre-coated substrates such as anodized aluminum or phosphate coated substrates to improve the adhesion bonding and corrosion-resistance properties of the metal. Phosphate coatings known in the art include, for example, coatings of zinc phosphate, iron phosphate, manganese phosphates and mixed calcium-zinc phosphate coatings. The process comprises using the acidic aqueous solution at temperatures ranging up to about 48.9°C (120°F) or higher e.g. up to about 93.3°C (200°F). The solutions comprise from about 0.01 to 100 grams and preferably from about 0.01 to 22 or 5.0 to 7.0 grams per liter of the acidic solution of at least one water soluble trivalent chromium compound e.g. chromium sulfate, about 0.01 to 24 grams and preferably about 1.0 to 12 or 1.0 to 6.0 grams per liter of the solution of at least one fluorozirconate e.g. an alkali metal salt of H_2ZrF_6, an effective amount sufficient to inhibit corrosion ranging, for example, from about 0.001 to 4.0 grams per liter and preferably about 0.25 to 2.0 grams or 0.25 to 1.0 gram per liter of a water-soluble corrosion inhibitor or anti-pitting compound such as benzotriazole, and from about 0.001 to 2.0 grams and preferably from 0.001 to 1.0 or 0.01 to 1.0 mole per liter of the solution of at least one water-soluble stabilizing agent or compound selected from the group consisting of carboxylic compounds, polyhydroxy compounds and mixtures of these stabilizing compounds in any ratio. If needed, each of the compounds of this invention can be used up to their solubility limits in the acidic aqueous solutions depending on the metal surface being treated. The metal surfaces treated in accordance with the present invention may be any metal substrate including, for example, iron, zinc, magnesium, steel surfaces including galvanized steel, aluminum and aluminum alloys. Any metal surface, including metal surfaces containing a protective or preexisting metal coating may be treated with the compositions of the present invention.

[0018] The coatings are applied after cleaning and deoxidizing or pickling the metal substrate e.g. aluminum substrate via conventional mechanical or chemical techniques. The acidic solution of this invention is applied at about room temperature to the metal substrate via immersion, spray or wipe-on techniques similar to the process used for other metal treatments. Solution dwell time ranges from about 1.0 to 60 minutes or longer. With this solution, the 1.0 to 40 or 1.0 to 10 minute dwell time yields an optimum film for color change, paint adhesion, and corrosion resistance. The 1.0 to 10 minute dwell time yields appreciable color change to the coating depending primarily on the chemical composition of the aqueous solution. The remaining solution is subsequently rinsed from the metal substrate with tap or deionized water.

[0019] In some processes, depending on the physical characteristics of the metal substrate e.g. the physical size of the steel or aluminum substrates, the addition of a thickener to the solution aids in optimum film formation during spray and wipe-on applications by slowing down solution evaporation. This mitigates the formation of powdery deposits that degrade paint adhesion. The addition of thickeners, also aids in proper film formation during large area applications and mitigates the diluent effect of rinse water that remains on the substrate during processing from previous steps. This feature of the process yields films or coatings that have no streaks and are an improvement in both coloration and corrosion protection. Water-soluble thickeners such as the cellulose compounds can be present in the acidic aqueous solution in amounts ranging from about 0.0 to 20 grams per liter and preferably 0.5 to 10 grams e.g., about 0.1 to 5.0 grams per liter of the aqueous solution. Further, depending on the characteristics of the metal substrates, an effective but small amount of at least one water-soluble surfactant or wetting agent can be added to the acidic solution in amounts ranging from about 0.0 to 20 grams and preferably from 0.5 to 10 grams e.g. 0.1 to 5.0 grams per liter of the acidic solution. There are many water soluble surfactants known in the prior art and therefore for purpose of this invention the surfactants can be selected from the group consisting of non-ionic, cationic and anionic surfactants.

[0020] The trivalent chromium is added to the solution as a water-soluble trivalent chromium compound, either as a liquid or solid and preferably as a trivalent chromium salt. Specifically, in formulating the acidic aqueous solutions of this invention, the chromium salt can be added conveniently to the solution in its water soluble form wherein the valence of the chromium is plus 3. For example, some of the preferred chromium compounds are incorporated in the solution in the form of $Cr_2(SO_4)_3$, $(NH_4)Cr(SO_4)_2$, $Cr(NO)_3$-$9H_2O$ or $KCr(SO_4)_2$ and any mixtures of these compounds. A preferred trivalent chromium salt concentration is within the range of about 5.0 to 7.0 grams per liter of the aqueous solution. It has been found that particularly good results are obtained from these processes when the trivalent chromium compound is present in solution in the preferred ranges.

[0021] The acidic solutions may contain at least one divalent zinc compound to provide color and also improve the corrosion protection of the metal when compared to other treatments or compositions that do not contain zinc. The amount of the zinc compounds can be varied up to the solubility limits to adjust the color imparted to the coating, ranging from 0.0 to 100 grams to as little as about 0.001 grams per liter up to 10 grams per liter e.g. 0.5 to 2.0 grams of $Zinc^{2}$+cation. The divalent zinc can be supplied by any chemical compound e.g. salt that dissolves in water at the required concentration and is compatible with the other components in the acid solution. Divalent zinc compounds that are water soluble at the required concentrations preferably include, for example, zinc acetate, zinc telluride, zinc tetrafluoroborate, zinc molybdate, zinc hexafluorosilicate, zinc sulfate and the like or any combination thereof in any ratio. The treatment or coating of the metal substrates can be carried out at various temperatures including temperatures of the solution which ranges from ambient e.g. from about room temperature up to about 48.9°C (120°F) or higher up to about 93.3°C (200°F). Room temperature is preferred, however, in that this eliminates the necessity for heating equipment. The coating may be air dried by any of the methods known in the art including, for example, oven drying, forced-air drying, exposure to infra-red lamps, and the like.

[0022] The following Examples illustrate the stable acidic solutions of this invention, and the method of using the solutions in providing color recognition, improved adhesion bonding and corrosion-resistant coatings for metal substrates including metal substrates having a preexisting metal coating.

EXAMPLE 1

[0023] To one liter of deionized water, add 4.0 grams of potassium hexafluorozirconate, 3.0 grams of chromium III sulfate basic, 0.12 grams potassium tetrafluoroborate, and 0.25 grams benzotriazole. Stir solution until all compounds are dissolved. Let stand at ambient conditions 521-27°C (70-80°F)) until pH reaches 3.70.

EXAMPLE 2

[0024] To one liter of deionized water, add 4.0 grams of potassium hexafluorozirconate, 3.0 grams of chromium III sulfate basic, 2.3 grams glycerol (0.025moles), and 0.25 grams benzotriazole. Stir solution until all compounds are dissolved. Let stand at ambient conditions (21-27°C) (70-80F)) until pH reaches 3.55.

EXAMPLE 3

[0025] To one liter of deionized water, add 4.0 grams of potassium hexafluorozirconate and 3.0 grams of chromium III sulfate basic. Stir solution until all compounds are dissolved. Maintain pH between 3.25 and 3.50 for 14 days with dilute sulfuric acid and dilute potassium hydroxide and then adjust to final pH of 3.90. Add 0.25 grams benzotriazole.

EXAMPLE 4

[0026] Prepare solution as in Example 2, except replace the benzotriazole with 0.50 grams of 2-mercaptobenzimidazole.

EXAMPLE 5

[0027] Prepare solution as in Example 3, except add 0.25 grams of 2-mercaptobenzimidazole in addition to the benzotriazole.

EXAMPLE 6

[0028] Prepare solution as in Example 1, except add 0.25 grams 2-mercaptobenzimidazole and 0.25 grams 2-mercaptobenzazole in addition to the benzotriazole.

EXAMPLE 7

[0029] The compositions of Examples 1,2 and 3 were used to coat the aluminum alloy (2024-T3) panels as follows:

[0030] The process comprises cleaning 76 mm by 127 mm by 0.77 mm (3 inch by 5 inch by 0.030 inch) (2024-T3) panels in Turco 425 at 60°C (140°F) for 15 minutes. Rinse in warm tap water using cascading double backflow. Immediately, immerse coupons in Turco Smut Go for 5 minutes. Rinse in ambient temperature tap water using cascading double backflow. Immediately, immerse the panels in the compositions of Examples 1, 2 and 3 for five (5) minutes at 21-27°C (70-80°F). Rinse in ambient temperature tap water using cascading double backflow. Final rinse with deionized water. Let the panels air dry and stand overnight. Coatings are ready for testing or subsequent coating with an organic finish coating e.g. (MIL-PRF-23377) epoxy primer.

EXAMPLE 8

[0031] Test panels were cleaned and coated by the process set forth in Example 7 then placed in neutral salt fog (ASTM B117) at an incline of 6 degrees from vertical. After 3 weeks (21 days) in salt fog, the coating performance is shown in Figures 1-6. Control coatings were made from the compositions of Examples 1,2 and 3 without the addition of the triazole pitting inhibitors. It is evident from comparing Figures 1-6 (photos) that the addition of the pitting inhibitors resulted in a positive effect on the corrosion resistance of the coatings made from the different compositions.

[0032] The anti-pitting or corrosion inhibitors are water-soluble compounds selected from the group consisting of triazoles, benzimidazoles, benzazoles, benzoxazoles and mixtures of these inhibitors in any ratio. The preferred corrosion inhibitors or anti-pitting compounds include the triazoles containing up to 12 carbon atoms, such as the alkyl and preferably the aryl triazoles. The aryl triazoles contain from 6-10 carbon atoms, including compounds such as benzotriazole and tolyltriazole, and the alkyl triazoles containing up to six carbons such as methyl or ethyl triazole. The triazoles such as benzotriazole are commercially available under the trade name COBRATEC. The anti-pitting inhibitors are dissolved in the solutions in an effective amount sufficient to inhibit corrosion, and preferably in amounts ranging from about 0.001 to 4.0 grams per liter, and more preferably in amounts of 0.25 to 2.0 grams or from about 0.25 to 1.0 grams per liter. Other useful triazoles include the water soluble hydroxybenzotriazole, such as hydroxy-4-alkylbenzotriazoles, hydroxy-6-benzotriazole, hydroxy-5-chlorobenzotriazole, hydroxy-6-carboxybenzotriazole, hydroxy-5-alkylbenzotriazoles and the like.

[0033] The stabilizing carboxylic compounds added to the acidic aqueous solutions include water-soluble acids and/or carboxylic acid salts, including the water-soluble carboxylic acids and salts such as adipic, citric, acetic, citraconic, fumaric, glutaric, tartaric acids, or ethylenediamine tetraacetic acid provided the hydrocarbon chain on the carboxylic group does not contain a significant number of carbons which decrease the compounds degree of solubility. Combinations of two or more of the salts and/or acids can be used to obtain a specific pH. For example, the lower molecular acids and/or salts such as potassium formate or citrate can be used at concentrations of at least 0.001 to 2.0 moles or 0.001 to 1.0 mole per liter. These compounds are good all-around stabilizers. Particularly good results were obtained from acidic solutions prepared by adding about 0.01 mole per liter of potassium formate after 4 days of the initial solution preparation. Good results are obtained if the stabilizing agents are carboxylic compounds containing both hydroxy and carboxylic groups including, for example, compounds such as citric acid, glycolic acid, lactic acid, gluconic acids, glutaric acid and their salts.

[0034] In addition to the carboxylic compounds as stabilizing agents for the solutions, small but effective amount of polyhydroxy compounds also can be used as stabilizers in amounts ranging from about 0.001 to 2.0 and preferably from 0.01 to 2.0 moles or 0.01 to 1.0 mole per liter. The compounds include the trihydric compounds e.g. glycerol and the dihydric ether alcohols e.g. glycol ethers including alkylene glycol ethers, such as triethylene glycol ether, propylene glycol ether, tripropyleneglycol ether, or diethyleneglycol ether. Other glycols include some of the lower molecular weight compounds such as ethylene glycol, propylene glycol, butylene glycol, cyclohexanol, and the water-soluble poly (oxyalkylene glycols) e.g. the poly-(oxyethylene) or poly-(oxypropylene glycols), having lower molecular weights ranging up to about 1000 may be employed to promote stability and dispersibility of solids in the coating bath or acid solutions. Other known di- and trihydric aliphatic alcohols include the water soluble lower alkanols, such as the di- and trihydric alkanols containing up to twelve carbon atoms. This class of di- and trihydric lower alkanols can include glycols containing up to ten carbon atoms in the alkylene group e.g. trimethylene glycol, and the polyglycols, such as diethylene glycol, triethylene glycol, tetraethylene glycol, dipropylene glycol, tripropylene glycol, dibutylene glycol, tributylene glycol, and other polyalkylene glycols wherein the alkylene radical contains up to eight carbon atoms and preferably from two to four carbon atoms. Combinations or mixtures of the carboxylic and polyhydroxy stabilizing compounds may be used in the acidic solution in any ratio. In addition to the polyhydroxy and carboxylic stabilizing compounds, the acidic aqueous solutions may contain small but effective amounts of from 0.0 to 24 grams e.g. 0.01 to 12 grams per liter of solution of at least one fluorometallic compound preferably including stabilizing compounds such as hexafluorotitanate, heptafluorotantalate, tetrafluoroborate and hexafluorosilicate.

[0035] In preparing the acidic solutions of this invention, known water soluble surfactants can be added to the trivalent chromium solutions in amounts ranging from about 0 to 20 grams per liter and preferably about 5.0 to 10 grams or 1.0 to 5.0 grams per liter. The surfactants are added to the aqueous solution to provide better wetting properties by lowering the surface tension thereby insuring complete coverage, and a more uniform film on the metal substrates. The surfactants include at least one water soluble compound selected from the group consisting of non-ionic, anionic, and cationic surfactants. Some of the better known water soluble surfactants include the monocarboxyl imidoazoline, alkylsulfate sodium salts (DUPONOL®), ethoxylated or propoxylated alkylphenol (IGEPAL®), alkylsulfonamides, alkaryl sulfonates, palmiticalkanol amides (CENTROL®), octylphenyl polyethoxy ethanol (TRITON®), sorbitan monopalmitate (SPAN®); dodecylphenyl polyethyleneglycol ether (TERGITROL®), alkyl pyrrolidones, polyalkoxylated fatty acid esters, alkylbenzene sulfonates and mixtures thereof. Other known water soluble surfactants include, for example, the nonylphenol ethoxylates, and adducts of ethylene oxide with fatty amines; see the publication: "Surfactants and Detersive Systems", by John Wiley et al. in Kirk-Othmer's Encyclopedia of Chemical Technology, 3rd Ed.

[0036] When large surfaces do not permit immersion or where vertical surfaces are to be sprayed, thickening agents can be added to retain the aqueous solution on the surface for sufficient contact time. The thickeners employed are known inorganic and preferably the organic water soluble thickeners added to the trivalent chromium solutions in effective amounts e.g. at sufficient concentrations ranging from about 0 to 20 grams per liter and preferably 0.5 to 10 grams or 1.0 to 5.0 grams per liter of the acidic solution. Specific examples of some preferred thickeners include the cellulose compounds, e.g. hydroxypropyl cellulose (Klucel), ethyl cellulose, hydroxyethyl cellulose, hydroxymethyl cellulose, methyl cellulose and mixtures thereof. Other water soluble inorganic thickeners include colloidal silica, clays such as bentonite, starches, gum arabic, tragacanth, agar and various combinations.

[0037] After preparing the metal substrate surface to be coated via conventional techniques, the solution can be applied via immersion, spray or wipe-on techniques. The TCP solutions of this invention can be used at elevated temperatures ranging up to 48.9°C (120°F) or higher e.g. up to 93.3°C (200°F) and optimally applied via immersion to further improve the corrosion resistance of the coatings. Solution dwell time ranges from about 1 to 60 minutes, and preferably 1.0 to 40 or 1.0 to 10 minutes at about 23.9°C (75°F) or higher. After dwelling, the remaining solution is then thoroughly rinsed from the substrate with tap or deionized water. No additional chemical manipulations of the deposited films are necessary for excellent performance. The aqueous solutions may be sprayed from a spray tank apparatus designed to replace immersion tanks.

Claims

1. Process for coating metal substrates to improve the corrosion protection and adhesion bonding strength of the metal which comprises treating the metal substrates with an acidic aqueous solution having a pH ranging from 1.0 to 5.5; said acidic aqueous solution

comprising, per liter of solution, from 0.01 to 100 grams of at least one trivalent chromium compound, from 0.01 to 24 grams of at least one fluorozirconate, from 0.0 to 100 grams of divalent zinc compounds, from 0.0 to 20 grams of surfactants, from 0.0 to 20 grams of thickeners,

characterized in that

said acidic aqueous solution further comprises 0.001 to 4.0 grams per liter of at least one water soluble corrosion inhibitor selected from the group consisting of triazoles, benzimidazoles, benzazoles and benzoxazoles, and 0.001 to 2.0 grams per liter of a stabilizing compound selected from the group consisting of polyhydroxy compounds, carboxylic compounds and mixtures of polyhydroxy and carboxylic compounds wherein said polyhydroxy compounds are selected from the group consisting of glycerol, methylene glycol ether, propylene glycol ether, tripropylene glycol ether, diethylene glycol ether, glycol, propylene glycol, butylene glycol, cyclohexanol, water-soluble poly(oxyethylene glycols) and poly (oxypropylene glycols) having molecular weights ranging up to about 1000, trimethylene glycol, diethylene glycol, methylene glycol, tetraethylene glycol, dipropylene glycol, tripropylene glycol, dibutylene glycol, tributylene glycol, and polyalkylene glycols wherein the alkylene radical contains up to eight carbon atoms, and wherein said carboxylic compounds are selected from the group consisting of formic, acetic, propionic, citric, adipic, citraconic, fumaric, glutaric, tartaric, lactic, glycolic, gluconic, and ethylenediamine tetraacetic acids and their salts.

2. The process of Claim 1 wherein the metal substrates have a pre-existing metal coating thereon.

3. The process of Claim 2 wherein the pre-existing metal coated substrate is at least one of an anodized aluminum and a phosphate coating.

4. The process of Claim 1 wherein the metal substrate is at least one of an aluminum alloy and an iron alloy.

5. The process of Claim 1 wherein the carboxylic compound is at least one of a hydroxy-carboxylic compound, a formic acid, a propionic acid and the water soluble salts thereof.

6. The process of Claim 1 wherein the water soluble corrosion inhibitor is benzotriazole.

7. The process of 5 wherein the hydroxy-carboxylic compound is at least one of a citric acid, a gluconic acid, a glycolic acid and the water soluble salts thereof.

8. The process of Claim 1 wherein the acidic aqueous solution contains from 0.001 to 1.0 mole per liter of the carboxylic compound and the inhibitor is a triazole.

9. The process of Claim 1 wherein the acidic aqueous solution contains from 0.001 to 2.0 moles per liter of the stabilizing compound and 0.025 to 4.0 grams per liter of a triazole.

10. The process of Claim 1 wherein the stabilizing compound is glycerol and the water soluble corrosion inhibitor is a mixture of benzotriazole and tolyltriazole.

11. The process of Claim 1 wherein the stabilizing compound is a carboxylic compound having more than one functional carboxylic group per molecule.

12. Compositions for coating metal substrates to improve the corrosion protection and adhesion bonding strength of said metal which comprise an acidic aqueous solution having a pH ranging from 1.0 to 5.5 and per liter of said solution from 0.01 to 100 grams of at least one trivalent chromium compound, from 0.01 to 24 grams of at least one fluorozirconate, from 0.0 to 20 grams of divalent zinc compounds, from 0.0 to 20 grams of surfactants, from 0.0 to 20 grams of thickeners,

characterized in that

said acidic aqueous solution further comprises 0.001 to 4.0 grams per liter of at least one water soluble corrosion inhibitor selected from the group consisting of triazoles, benzimidazoles, benzazoles and benzoxazoles and mixtures of said inhibitors, and 0.001 to 2.0 grams per liter of a stabilizing compound selected from the group consisting of polyhydroxy compounds, carboxylic compounds and mixtures of polyhydroxy and carboxylic compounds, wherein said polyhydroxy compounds are selected from the group consisting of glycerol, methylene glycol ether, propylene glycol ether, tripropylene glycol ether, diethylene glycol ether, glycol, propylene glycol, butylene glycol, cyclohexanol, water-soluble poly(oxyethylene glycols) and poly(oxypropylene glycols) having molecular weights ranging up to about 1000, trimethylene glycol, diethylene glycol, methylene glycol, tetraethylene glycol, dipropylene glycol, tripropylene glycol, dibutylene glycol, tributylene glycol, and polyalkylene glycols wherein the alkylene radical contains up to eight carbon atoms, and wherein said carboxylic compounds are selected from the group consisting of formic, acetic, propionic, citric, adipic, citraconic, fumaric, glutaric, tartaric, lactic, glycolic, gluconic, and ethylenediamine tetraacetic acids and their salts.

13. The composition of Claim 12 wherein the stabilizing compound is a carboxylic compound having more than one functional carboxylic group per molecule.

14. The composition of Claim 13 wherein the carboxylic compound is a hydroxy-carboxylic acid and the water soluble salts thereof.

15. The composition of Claim 14 wherein the hydroxy-carboxylic compound is selected from the group consisting of citric acid, glycolic acid, lactic acid, the water soluble salts thereof and combinations thereof.

16. The composition of Claim 12 wherein the carboxylic compound is at least one of a formic acid, propionic acid and the water soluble salts thereof.

17. The composition of Claim 12 wherein the polyhydroxy compound is glycerol, the carboxylic compound is a lower molecular weight carboxylic acid or a water soluble salt thereof and the water soluble corrosion inhibitor is a triazole.

18. The composition of Claim 12 wherein the stabilizing compound is a mixture of a lower molecular weight carboxylic acid and a polyhydroxy compound.

19. The composition of Claim 12 wherein the stabilizing compound is a low molecular weight polyhydroxy compound and the water soluble corrosion inhibitor is mercaptobenzimidazole.

20. The composition of Claim 12 wherein the polyhydroxy compound is glycerol and the water soluble corrosion inhibitor is at least one of a benzotriazole and a mixture of triazoles.

21. The composition of Claim 12 wherein the divalent zinc compound is a water soluble zinc salt present in the acidic aqueous solution in an amount ranging from 0.5 to 2.0 grams and the water soluble corrosion inhibitor is at least one of a benzotriazole and a mercaptobenzazole.

22. The composition of Claim 12 wherein the polyhydroxy compound is a polyalkylene glycol and the water soluble corrosion inhibitor is benzimidazole.

23. The composition of Claim 12 wherein the pH ranges from 2.5 to 4.5, the trivalent chromium compound ranges from 0.01 to 22 grams, the fluorozirconate is hexafluorozirconate ranging from 1.0 to 12 grams, the stabilizing compounds range from 0.001 to 1.0 mole per liter, and the inhibitor is a triazole ranging from 0.001 to 4.0 grams per liter of solution.

24. The composition of Claim 23 wherein the stabilizing compound is a lower molecular weight carboxylic acid or a water soluble salt thereof and the triazole is tolyltriazole.

25. The composition of Claim 12 wherein the stabilizing compound is a polyhydroxy compound and the water soluble corrosion inhibitor is mercaptobenzazole.

26. The composition of Claim 12 wherein the divalent zinc compound ranges from 0.001 to 10 grams and the water soluble corrosion inhibitor is a benzazole.

27. The composition of Claim 12 wherein the thickeners and/or the surfactants range from 1.0 to 5.0 grams and the water soluble corrosion inhibitor is mercaptobenzoxazole.

28. The composition of Claim 12 wherein the acidic aqueous solution contains from 0.01 to 12 grams per liter of at least one fluorometallic compound selected from the group consisting of fluorotitanates, fluorotantalates, fluoroborates, fluorosilicates and mixtures thereof and the water soluble corrosion inhibitor is a mixture of said inhibitors.

29. The composition of Claim 28 wherein the fluorometallic compound is at least one of a hexafluorosilicate and a tetrafluoroborate, the fluorozirconate is hexafluorozirconate and the water soluble corrosion inhibitor is at least one of a tolyltriazole and a benzotriazole.

Patentansprüche

1. Verfahren zum Beschichten von Metallsubstraten zur Verbesserung des Korrosionsschutzes und der Haftfestigkeit des Metalls, welches ein Behandeln der Metallsubstrate mit einer sauren wässrigen Lösung mit einem pH von 1,0 bis 5,5 umfasst; wobei die saure wässrige Lösung pro Liter der Lösung von 0,01 bis 100 Gramm von mindestens einer dreiwertigen Chromverbindung, von 0,01 bis 24 Gramm von mindestens einem Fluorzirconat, von 0,0 bis 100 Gramm an zweiwertigen Zinkverbindungen, von 0,0 bis 20 Gramm an Tensiden, von 0,0 bis 20 Gramm an Verdickungsmitteln umfasst,
dadurch gekennzeichnet, dass
die saure wässrige Lösung ferner 0,001 bis 4,0 Gramm pro Liter an mindestens einem wasserlöslichen Korrosionsinhibitor, der aus der Gruppe ausgewählt ist bestehend aus Triazolen, Benzimidazolen, Benzazolen und Benzoxazolen, und 0,001 bis 2,0 Gramm pro Liter einer Stabilisierungsverbindung, die aus der Gruppe ausgewählt ist bestehend aus Polyhydroxyverbindungen, Carboxylverbindungen und Mischungen von Polyhydroxy- und Carboxylverbindungen, umfasst, wobei die Polyhydroxyverbindungen aus der Gruppe ausgewählt sind bestehend aus Glycerol, Methylenglycolether, Propylenglycolether, Tripropylenglycolether, Diethylenglycolether, Glycol, Propylenglycol, Butylenglycol, Cyclohexanol, wasserlöslichen Poly(oxyethylenengly-

colen) und Poly(oxypropylenglycolen) mit Molekulargewichten von bis zu ungefähr 1000, Trimethylenglycol, Diethylenglycol, Methylenglycol, Tetraethylenglycol, Dipropylenglycol, Tripropylenglycol, Dibutylenglycol, Tributylenglycol und Polyalkylenglycolen, wobei der Alkylenrest bis zu acht Kohlenstoffatome enthält, und wobei die Carboxylverbindungen aus der Gruppe ausgewählt sind bestehend aus Ameisen-, Essig-, Propion-, Zitronen-, Adipin-, Citracon-, Fumar-, Glutar-, Wein-, Milch-, Glycol-, Glucon- und Ethylendiamintetraessigsäure und deren Salzen.

2. Verfahren nach Anspruch 1, wobei die Metallsubstrate eine bereits darauf vorhandene Metallbeschichtung aufweisen.

3. Verfahren nach Anspruch 2, wobei das Metallsubstrat mit bereits vorhandener Metallbeschichtung mindestens eines von einem anodisierten Aluminium und einer Phosphatbeschichtung ist.

4. Verfahren nach Anspruch 1, wobei das Metallsubstrat mindestens eines von einer Aluminiumlegierung und einer Eisenlegierung ist.

5. Verfahren nach Anspruch 1, wobei die Carboxylverbindung mindestens eine von einer Hydroxycarboxylverbindung, einer Ameisensäure, einer Propionsäure und deren wasserlöslichen Salzen ist.

6. Verfahren nach Anspruch 1, wobei der wasserlösliche Korrosionsinhibitor Benzotriazol ist.

7. Verfahren nach Anspruch 5, wobei die Hydroxycarboxylverbindung mindestens eine von einer Zitronensäure, einer Gluconsäure, einer Glycolsäure und deren wasserlöslichen Salzen ist.

8. Verfahren nach Anspruch 1, wobei die saure wässrige Lösung von 0,001 bis 1,0 mol pro Liter der Carboxylverbindung enthält und der Inhibitor ein Triazol ist.

9. Verfahren nach Anspruch 1, wobei die saure wässrige Lösung von 0,001 bis 2,0 mol pro Liter der Stabilisierungsverbindung und 0,025 bis 4,0 Gramm pro Liter eines Triazols enthält.

10. Verfahren nach Anspruch 1, wobei die Stabilisierungsverbindung Glycerol ist und der wasserlösliche Korrosionsinhibitor eine Mischung aus Benzotriazol und Tolyltriazol ist.

11. Verfahren nach Anspruch 1, wobei die Stabilisierungsverbindung eine Carboxylverbindung mit mehr als einer funktionellen Carboxylgruppe pro Molekül ist.

12. Zusammensetzungen zum Beschichten von Metallsubstraten zur Verbesserung des Korrosionsschutzes und der Haftfestigkeit des Metalls, welche eine saure wässrige Lösung mit einem pH von 1,0 bis 5,5 und pro Liter der Lösung von 0,01 bis 100 Gramm von mindestens einer dreiwertigen Chromverbindung, von 0,01 bis 24 Gramm von mindestens einem Fluorzirconat, von 0,0 bis 20 Gramm an zweiwertigen Zinkverbindungen, von 0,0 bis 20 Gramm an Tensiden, von 0,0 bis 20 Gramm an Verdickungsmitteln umfassen,

dadurch gekennzeichnet, dass

die saure wässrige Lösung ferner 0,001 bis 4,0 Gramm pro Liter an mindestens einem wasserlöslichen Korrosionsinhibitor, der aus der Gruppe ausgewählt ist bestehend aus Triazolen, Benzimidazolen, Benzazolen und Benzoxazolen und Mischungen der Inhibitoren, und 0,001 bis 2,0 Gramm pro Liter einer Stabilisierungsverbindung, die aus der Gruppe ausgewählt ist bestehend aus Polyhydroxyverbindungen, Carboxylverbindungen und Mischungen von Polyhydroxy- und Carboxylverbindungen, umfasst, wobei die Polyhydroxyverbindungen aus der Gruppe ausgewählt sind bestehend aus Glycerol, Methylenglycolether, Propylenglycolether, Tripropylenglycolether, Diethylenglycolether, Glycol, Propylenglycol, Butylenglycol, Cyclohexanol, wasserlöslichen Poly-(oxyethylenglycolen) und Poly(oxypropylenglycolen) mit Molekulargewichten von bis zu ungefähr 1000, Trimethylenglycol, Diethylenglycol, Methylenglycol, Tetraethylenglycol, Dipropylenglycol, Tripropylenglycol, Dibutylenglycol, Tributylenglycol und Polyalkylenglycolen, wobei der Alkylenrest bis zu acht Kohlenstoffatome enthält, und wobei die Carboxylverbindungen aus der Gruppe ausgewählt sind bestehend aus Ameisen-, Essig-, Propion-, Zitronen-, Adipin-, Citracon-, Fumar-, Glutar-, Wein-, Milch-, Glycol-, Glucon- und Ethylendiamintetraessigsäure und deren Salzen.

13. Zusammensetzung nach Anspruch 12, wobei die Stabilisierungsverbindung eine Carboxylverbindung mit mehr als einer funktionellen Carboxylgruppe pro Molekül ist.

14. Zusammensetzung nach Anspruch 13, wobei die Carboxylverbindung eine Hydroxycarboxylverbindung und die wasserlöslichen Salze davon ist.

15. Zusammensetzung nach Anspruch 14, wobei die Hydroxycarboxylverbindung aus der Gruppe ausgewählt ist bestehend aus Zitronensäure, Glycolsäure, Milchsäure, deren wasserlöslichen Salzen und deren Kombinationen.

16. Zusammensetzung nach Anspruch 12, wobei die Carboxylverbindung mindestens eine von einer Ameisensäure, Propionsäure und deren wasserlöslichen Salzen ist.

17. Zusammensetzung nach Anspruch 12, wobei die Polyhydroxyverbindung Glycerol ist, die Carboxylverbindung eine Carbonsäure mit niedrigem Molekulargewicht oder ein wasserlösliches Salz davon ist und der wasserlösliche Korrosionsinhibitor ein Triazol ist.

18. Zusammensetzung nach Anspruch 12, wobei die Stabilisierungsverbindung eine Mischung aus einer Carbonsäure mit niedrigem Molekulargewicht und einer Polyhydroxyverbindung ist.

19. Zusammensetzung nach Anspruch 12, wobei die Stabilisierungsverbindung eine Polyhydroxyverbindung mit niedrigem Molekulargewicht ist und der wasserlösliche Korrosionsinhibitor Mercaptobenzimidazol ist.

20. Zusammensetzung nach Anspruch 12, wobei die Polyhydroxyverbindung Glycerol ist und der wasserlöslich Korrosionsinhibitor mindestens eines von einem Benzotriazol und einer Mischung aus Triazolen ist.

21. Zusammensetzung nach Anspruch 12, wobei die zweiwertige Zinkverbindung ein wasserlösliches Zinksalz ist, das in der sauren wässrigen Lösung in einer Menge von 0,5 bis 2,0 Gramm vorhanden ist, und der wasserlösliche Korrosionsinhibitor mindestens eines von einem Benzotriazol und einem Mercaptobenzazol ist.

22. Zusammensetzung nach Anspruch 12, wobei die Polyhydroxyverbindung ein Polyalkylenglycol ist und der wasserlösliche Korrosionsinhibitor Benzimidazol ist.

23. Zusammensetzung nach Anspruch 12, wobei der pH von 2,5 bis 4,5 reicht, die dreiwertige Chromverbindung von 0,01 bis 22 Gramm reicht, das Fluorzirconat Hexafluorzirconat ist, das von 1,0 bis 12 Gramm reicht, die Stabilisierungsverbindungen von 0,001 bis 1,0 mol pro Liter reichen und der Inhibitor ein Triazol ist, das von 0,001 bis 4,0 Gramm pro Liter der Lösung reicht.

24. Zusammensetzung nach Anspruch 23, wobei die Stabilisierungsverbindung eine Carbonsäure mit niedrigem Molekulargewicht oder ein wasserlösliches Salz davon ist und das Triazol Tolyltriazol ist.

25. Zusammensetzung nach Anspruch 12, wobei die Stabilisierungsverbindung eine Polyhydroxyverbindung ist und der wasserlösliche Korrosionsinhibitor Mercaptobenzazol ist.

26. Zusammensetzung nach Anspruch 12, wobei die zweiwertige Zinkverbindung von 0,001 bis 10 Gramm reicht und der wasserlösliche Korrosionsinhibitor ein Benzazol ist.

27. Zusammensetzung nach Anspruch 12, wobei die Verdickungsmittel und/oder die Tenside von 1,0 bis 5,0 Gramm reichen und der wasserlösliche Korrosionsinhibitor Mercaptobenzoxazol ist.

28. Zusammensetzung nach Anspruch 12, wobei die saure wässrige Lösung von 0,01 bis 12 Gramm pro Liter von mindestens einer Fluormetallverbindung enthält, die aus der Gruppe ausgewählt ist bestehend aus Fluortitanaten, Fluortantalaten, Fluorboraten, Fluorsilicaten und deren Mischungen, und der wasserlösliche Korrosionsinhibitor eine Mischung aus den Inhibitoren ist.

29. Zusammensetzung nach Anspruch 28, wobei die Fluormetallverbindung mindestens eine von einem Hexafluorsilicat und einem Tetrafluorborat ist, das Fluorzirconat Hexafluorzirconat ist und der wasserlöstiche Korrosionsinhibitor mindestens eines von einem Tolyltriazol und einem Benzotriazol ist.

Revendications

1. Procédé de revêtement de substrats métalliques pour améliorer la protection contre la corrosion et la résistance de liaison par adhérence du métal, qui comprend le traitement des substrats métalliques avec une solution aqueuse acide ayant, un pH de l'ordre de 1,0 à 5,5 ; ladite solution aqueuse acide comprenant par litre de solution, de 0,01 à 100 grammes d'au moins un composé de chrome trivalent, de 0,01 à 24 grammes d'au moins un fluorozirconate, de 0,0 à 100 grammes de composés de zinc divalents, de 0,0 à 20 grammes de tensioactifs, de 0,0 à 20 grammes d'épaississants,
caractérisé en ce que
ladite solution acide comprend en outre 0,001 à 4,0 grammes par litre d'au moins un inhibiteur de corrosion hydrosoluble choisi dans le groupe comprenant des triazoles, des benzimidazoles, des benzazoles et des benzoxazoles, et 0,001 à 2,0 grammes par litre d'un composé stabilisant choisi dans le groupe comprenant des composés polyhydroxy, des composés carboxyliques et des mélanges de composés polyhydroxy et carboxyliques, lesdits' composés polyhydroxy étant choisis dans le groupe comprenant le glycérol, l'éther de méthylène glycol, l'éther de propylène glycol, l'éther de tripropylène glycol, l'éther de diéthylène glycol, le glycol, le propylène glycol, le butylène glycol, le cyclohexanol, les poly(oxyéthylène glycols) hydrosolubles et les poly(oxypropylène glycols) ayant des poids moléculaire allant jusqu'à

environ 1000, le triméthylène glycol, le diéthylène glycol, le méthylène glycol, le tétraéthylène glycol, le dipropylène glycol, le tripropylène glycol, le dibutylène glycol, le tributylène glycol et les polyalkylène glycols, le radical alkylène contenant jusqu'à huit atomes de carbone et lesdits composés carboxyliques étant choisis dans le groupe comprenant les acides formique, acétique, propionique, citrique, adipique, citraconique, fumarique, glutarique, tartrique, lactique, glycolique, gluconique et éthylène diamine tétra-acétique et leurs sels.

2. Procédé selon la revendication 1, dans lequel les substrats métalliques ont un revêtement métallique préexistant sur ceux-ci.

3. Procédé selon la revendication 2, dans lequel le substrat revêtu de métal préexistant est au moins un substrat parmi un revêtement d'aluminium anodisé et un revêtement de phosphate.

4. Procédé selon la revendication 1, dans lequel le substrat métallique est au moins un substrat parmi un alliage d'aluminium et un alliage de fer.

5. Procédé selon la revendication 1, dans lequel le composé carboxylique est au moins un composé parmi un composé hydroxy-carboxylique, un acide formique, un acide propionique et les sels hydrosolubles de ceux-ci.

6. Procédé selon la revendication 1, dans lequel l'inhibiteur de corrosion hydrosoluble est le benzotriazole.

7. Procédé selon la revendication 5, dans lequel le composé hydroxy-carboxylique est au moins un composé parmi un acide citrique, un acide gluconique, un acide glycolique et les sels hydrosolubles de ceux-ci.

8. Procédé selon la revendication 1, dans lequel la solution aqueuse acide contient de 0,001 à 1,0 mole par litre de composé carboxylique et l'inhibiteur est un triazole.

9. Procédé selon la revendication 1, dans lequel la solution aqueuse acide contient de 0,001 à 2,0 moles par litre de composé stabilisant et 0,025 à 4,0 grammes par litre d'un triazole.

10. Procédé selon la revendication 1, dans lequel le composé stabilisant est le glycérol et l'inhibiteur de corrosion hydrosoluble est un mélange de benzotriazole et de tolyltriazole.

11. Procédé selon la revendication 1, dans lequel le composé stabilisant est un composé carboxylique ayant plus d'un groupe carboxylique fonctionnel par molécule.

12. Compositions de revêtement de substrats métalliques pour améliorer la protection contre la corrosion et la résistance de liaison par adhérence dudit métal, qui comprennent une solution aqueuse acide ayant un pH de l'ordre de 1,0 à 5,5 et par litre de ladite solution, de 0,01 à 100 grammes d'au moins un composé de chrome trivalent, de 0,01 à 24 grammes d'au moins un fluorozirconate, de 0,0 à 20 grammes de composés de zinc divalents, de 0,0 à 20 grammes de tensioactifs, de 0,0 à 20 grammes d'épaississants,
caractérisées en ce que
ladite solution aqueuse acide comprend en outre de 0,001 à 4,0 grammes par litre d'au moins un inhibiteur de corrosion hydrosoluble choisi dans le groupe comprenant des triazoles, des benzimidazoles, des benzazoles et des benzoxazoles et des mélanges desdits inhibiteurs, et de 0,001 à 2,0 grammes par litre d'un composé stabilisant choisi dans le groupe comprenant des composés polyhydroxy, des composés carboxyliques et des mélanges de composés polyhydroxy et carboxyliques, lesdits composés polyhydroxy étant choisis dans le groupe comprenant le glycérol, l'éther de méthylène glycol, l'éther de propylène glycol, l'éther de tripropylène glycol, l'éther de diéthylène glycol, le glycol, le propylène glycol, le butylène glycol, le cyclohexanol, les poly(oxyéthylène glycols) hydrosolubles et les poly(oxypropylène glycols) ayant des poids moléculaire allant jusqu'à environ 1000, le triméthylène glycol, le diéthylène glycol, le méthylène glycol, le tétraéthylène glycol, le dipropylène glycol, le tripropylène glycol, le dibutylène glycol, le tributylène glycol et les polyalkylène glycols, le radical alkylène contenant jusqu'à huit atomes de carbone et lesdits composés carboxyliques étant choisis dans le groupe comprenant les acides formique, acétique, propionique, citrique, adipique, citraconique, fumarique, glutarique, tartrique, lactique, glycolique, gluconique et éthylène diamine tétra-acétique et leurs sels.

13. Composition selon la revendication 12, dans laquelle le composé stabilisant est un composé carboxylique ayant plus d'un groupe carboxylique fonctionnel par molécule.

14. Composition selon la revendication 13, dans laquelle le composé carboxylique est un acide hydroxy-carboxylique et les sels hydrosolubles de celui-ci.

15. Composition selon la revendication 14, dans laquelle le composé hydroxy-carboxylique est choisi dans le groupe comprenant l'acide citrique, l'acide glycolique, l'acide lactique, les sels hydrosolubles de ceux-ci et leurs combinaisons.

16. Composition selon la revendication 12, dans laquelle le composé carboxylique est au moins un composé parmi un acide formique, un acide propionique et les sels hydrosolubles de ceux-ci.

17. Composition selon la revendication 12, dans laquelle le composé polyhydroxy est le glycérol, le composé carboxylique est un acide carboxylique de poids moléculaire inférieur ou un sel hydrosoluble de celui-ci et l'inhibiteur de corrosion hydrosoluble est un triazole.

18. Composition selon la revendication 12, dans laquelle le composé stabilisant est un mélange d'un acide carboxylique à poids moléculaire inférieur et d'un composé polyhydroxy.

19. Composition selon la revendication 12, dans laquelle le composé stabilisant est un composé polyhydroxy de bas poids moléculaire et l'inhibiteur de corrosion hydrosoluble est le mercaptobenzimidazole.

20. Composition selon la revendication 12, dans laquelle le composé polyhydroxy est le glycérol et l'inhibiteur de corrosion hydrosoluble est au moins un benzotriazole et un mélange de triazoles.

21. Composition selon la revendication 12, dans laquelle le composé de zinc divalent est un sel de zinc hydrosoluble présent dans la solution aqueuse acide en une quantité allant de 0,5 à 2,0 grammes et l'inhibiteur de corrosion hydrosoluble est au moins un inhibiteur parmi un benzotriazole et un mercaptobenzazole.

22. Composition selon la revendication 12, dans laquelle le composé polyhydroxy est un polyalkylène glycol et l'inhibiteur de corrosion hydrosoluble est le benzimidazole.

23. Composition selon la revendication 12, dans laquelle le pH va de 2,5 à 4,5, le composé de chrome trivalent va de 0,01 à 22 grammes, le fluorozirconate est un hexafluorozirconate allant de 1,0 à 12 grammes, les composés stabilisants vont de 0,001 à 1,0 mole par litre et l'inhibiteur est un triazole allant de 0,001 à 4,0 grammes par litre de solution.

24. Composition selon la revendication 23, dans laquelle le composé stabilisant est un acide carboxylique de poids moléculaire inférieur ou un sel hydrosoluble de celui-ci et le triazole est le tolyltriazole.

25. Composition selon la revendication 12, dans laquelle le composé stabilisant est un composé polyhydroxy et l'inhibiteur de corrosion hydrosoluble est le mercaptobenzazole.

26. Composition selon la revendication 12, dans laquelle le composé de zinc divalent va de 0,001 à 10 grammes et l'inhibiteur de corrosion hydrosoluble est un benzazole.

27. Composition selon la revendication 12, dans laquelle les épaississants et/ou les tensioactifs vont de 1,0 à 5,0 grammes et l'inhibiteur de corrosion hydrosoluble est le mercaptobenzazole.

28. Composition selon la revendication 12, dans laquelle la solution aqueuse acide contient de 0,01 à 12 grammes par litre d'au moins un composé fluorométallique choisi dans le groupe comprenant les fluorotitanates, les fluorotantalates, les fluoroborates, les fluorosilicates et leurs mélanges et l'inhibiteur de corrosion hydrosoluble est un mélange desdits inhibiteurs.

29. Composition selon la revendication 28, dans laquelle le composé fluorométallique est au moins un composé parmi un hexafluorosilicate et un tétrafluoroborate, le fluorozirconate est un hexafluorozirconate et l'inhibiteur de corrosion hydrosoluble est au moins un inhibiteur parmi un tolyltriazole et un benzotriazole.

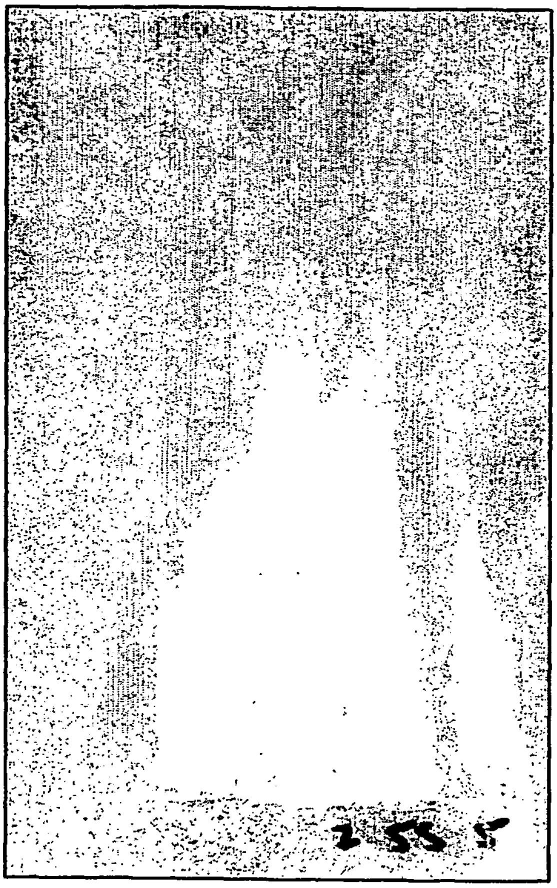

FIG-1

FIG-2

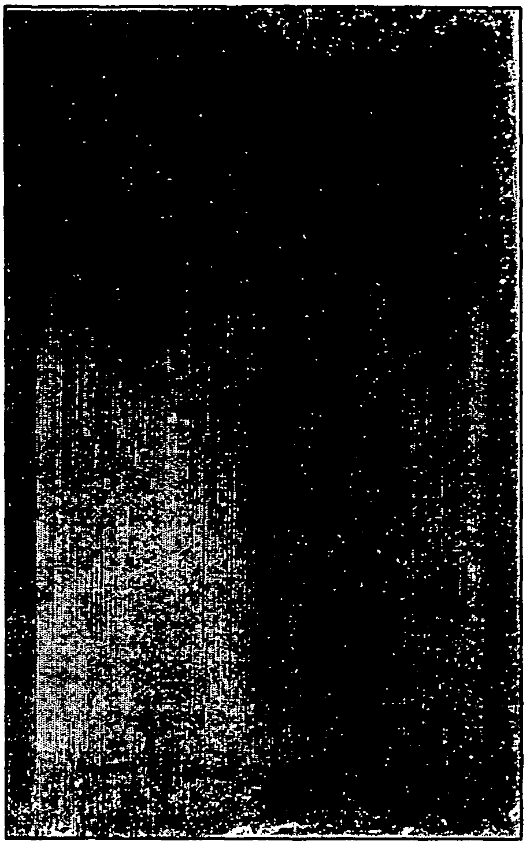

FIG-3

FIG-4

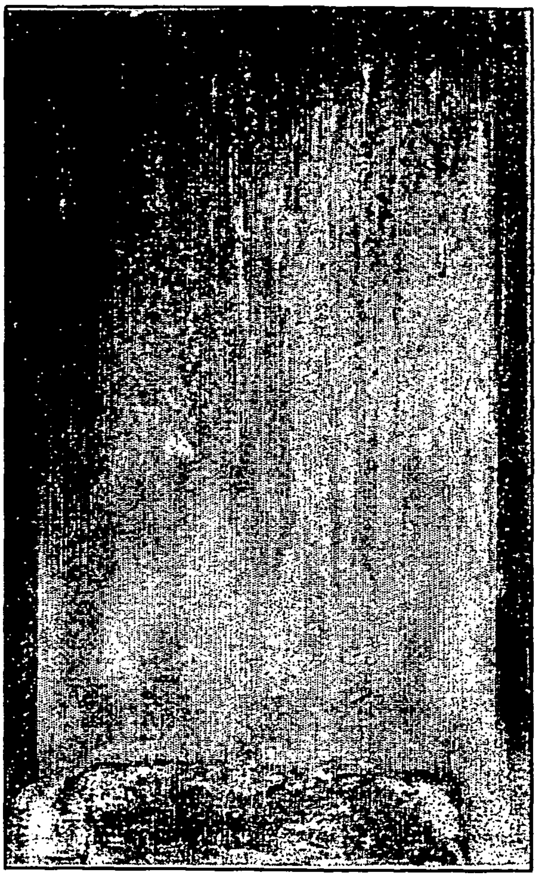

FIG-5

FIG-6

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- WO 03040431 A2 **[0005]**
- WO 03040437 A1 **[0005]**
- US 6669764 B1 **[0005]**
- US 2004054044 A1 **[0006]**
- US 4578122 A **[0007]**