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Description

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] The present invention relates to a method for forming a conversion coating on metal surfaces or substrates.

Background of the Related Art

[0002] In general, chemical conversion coatings are formed chemically by causing the surface of the metal to be "converted" into a tightly adherent coating, where either all or part of the conversion coating consists of an oxidized form of the substrate metal. Chemical conversion coatings can provide high corrosion resistance to the substrate as well as strong bonding affinity for paint. The industrial application of paint to metals generally requires the use of a chemical conversion coating, particularly when the performance demands are high.

[0003] Although aluminum protects itself against corrosion by forming a natural oxide coating, the protection is not complete. In the presence of moisture and electrolytes, aluminum alloys, particularly aluminum alloys with a high copper content, corrode much more rapidly than pure aluminum.

[0004] In general, there are two types of processes for treating aluminum to form a beneficial conversion coating. The first is by anodic oxidation (anodization) in which the aluminum component is immersed in a chemical bath, such as a chromic or sulfuric acid bath, and an electric current is passed through the aluminum component and the chemical bath. The conversion coating formed on the surface of the aluminum component offers resistance to corrosion and a bonding surface for organic finishes.

[0005] The second type of process is by chemically producing a conversion coating, which is commonly referred to as a chemical conversion coating, by subjecting the aluminum component to a chemical solution, such as a chromic acid solution, but without using an electric current in the process. The chemical solution may be applied by immersion application, by manual application, or by spray application. The resulting conversion coating on the surface of the aluminum component offers resistance to corrosion and a bonding surface for organic finishes.

[0006] Chromate based conversion coatings have been widely used in applications where maximum corrosion protection is an issue. Immersion of aluminum or aluminum alloys in a chromate conversion coating bath results in a thick, corrosion resistant film consisting of hydrated Cr(III) and Al(III) oxides. The reaction is driven by reduction of the high valent Cr(VI) ion and oxidation of the Al metal. Some of the benefits of a chromate conversion coating include hydrophobicity and self-healing properties.

[0007] Many aluminum structural parts, as well as Cd plated, Zn plated, Zn-Ni plated, and steel parts, throughout the aircraft and aerospace industry are currently being treated using this chromic acid process technology. Chromic acid conversion films, as formed on aluminum substrates, have been shown to meet a 168-hour corrosion resistance criterion, but they primarily serve as a surface substrate for paint adhesion. Because of their relative thinness and low coating weights (40-150 milligrams/ft²), chromic acid conversion coatings do not reduce the fatigue life of the aluminum structure.

[0008] However, environmental regulations in the United States, particularly in California, and in other countries are drastically reducing the levels of hexavalent chromium compounds permitted in effluents and emissions from metal finishing processes. Accordingly, chemical conversion coating processes employing hexavalent chromium compounds need to be replaced.

[0009] Some of the most investigated non-chromate conversion coatings used in treatment of aluminum alloy-based materials are described below.

[0010] Sol-Gel technology uses polymers or metal oxides either alone or mixed to form complexes by the hydrolysis of appropriate precursor compounds. Sol-Gels can form powders or thin films that inhibit corrosion on substrates.

[0011] Fluorozirconium coating technology uses complexed transition metal salts to create a thin film on a substrate material similar to a conversion coating. Specifically, zirconium is mixed with fluorine to create fluoro-zirconium, which reacts with the part surface to form a coating.

[0012] Cobalt-based coatings use cobalt and molybdenum to treat substrate materials. The coatings created are low in electrical resistance and are good for corrosion resistance.

[0013] Rare Earth Metal (REM) salts may be applied by heated immersion to create protective layers on substrate materials. REMs provide corrosion resistance by producing a protective oxide film.

[0014] Potassium permanganate solutions can be used to create manganese oxide films on substrates. Manganese oxide films resulting from potassium permanganate treatment closely match the corrosion resistance of traditional chromic oxide films used in conversion coatings. Potassium permanganate coatings are very effective in protecting aluminum alloys.

[0015] Fluorotitanic coatings, deposited from acid solutions with organic polymers, require few process steps, and can usually be done at ambient temperatures. Although these coatings have been widely used in a variety of applications, they have not been used in the aerospace industry.

[0016] Talc coatings, which are typically applied to aluminum substrates, are resistant to corrosion. These polycrystalline coatings are applied by precipitating aluminum-lithium compounds and other anions in an alka-
line salt solution.

[0017] Anodizing is a process in which a metal surface is converted to an oxide layer, producing a tough, adherent surface layer. A thick oxide layer can be produced by immersing a part in an electrolytic solution and passing an electrical current through it, similar to electroplating. Then, by placing the part in boiling water, the film's pores can be sealed. As a result, the oxide changes from one form to another.

[0018] Despite these alternatives, there is a continuing need for a conversion coating solution that will form a stable, corrosion-resistant conversion coating on metal surfaces without containing or producing toxic chemicals. There is also a need for a conversion coating solution that provides enhanced corrosion protection on a variety of substrate materials and under a variety of conditions. Additionally, it would be desirable if the conversion coating provided a suitable surface for receiving organic coatings or paints.

[0019] US-A-2,850,416 discloses a composition and process for treating metals, such as steel or aluminium, using a solution containing 0.5-5% ferrate (VI) and having a pH of 7-11. The solution contains preferably sodium salts as a buffer or stabiliser.


[0021] According to one aspect of this invention there is provided a solution for forming a conversion coating on a metal surface, the solution comprising ferrate (V1) (FeO₄²⁻) anions having a concentration of 1-100 mmol/l and one or more transition metal oxyanions selected from the group consisting of permanganate, molybdate, vanadate, tungstate and combinations thereof and wherein the solution has a pH greater than 13.5.

[0022] According to another aspect of this invention there is provided a solution for forming a conversion coating on a metal surface, the solution comprising ferrate (V1) (FeO₄²⁻) anions having a concentration of 1-100 mmol/l and one or more transition metal oxyanions selected from the group consisting of permanganate, molybdate, vanadate, tungstate and combinations thereof and wherein the solution has a pH between 13 and 13.5.

[0023] Preferably the solution further comprises one or more additional oxidising agents selected from the group consisting of peroxide, hypochlorite, ozone and combinations thereof.

[0024] Advantageously the ferrate (VI) oxyanion is provided by a compound selected from a sodium ferrate (VI) salt, a potassium ferrate (VI) salt, a solution of ferrate (VI) in potassium hydroxide, and mixtures thereof.

[0025] Preferably the solution further comprises ethylenediaminetetraacetic acid.

[0026] Advantageously the solution further comprises a salt selected from an alkali metal, or an alkaline earth metal, nitrate, chloride, fluoride or combinations thereof.

[0027] The invention also relates to a method for treating a metal surface, comprising cleaning and deoxidising the metal surface, rinsing the deoxidising metal surface with water, contacting the deoxidised and rinsing metal surface with an aqueous oxidising solution at a temperature in the range of 25-100°C, allowing the metal surface to be oxidised by the oxidising solution, and removing the oxidised metal surface from being in contact with the solution, characterised in that the oxidising solution is an aqueous solution comprising ferrate (VI) (FeO₄²⁻) having a concentration of 1-100 mmol/l and one or more transition metal oxyanions selected from the group consisting of permanganate, molybdate, vanadate, tungstate and, combinations thereof and wherein the solution has a pH greater than 13.5.

[0028] In another aspect the invention provides a method for treating a metal surface, comprising cleaning and deoxidising the metal surface, rinsing the deoxidising metal surface with water, contacting the deoxidised and rinsing metal surface with an aqueous oxidising solution at a temperature in the range of 25-100°C, allowing the metal surface to be oxidised by the oxidising solution, and removing the oxidised metal surface from being in contact with the solution, characterised in that the oxidising solution is an aqueous solution comprising ferrate (VI) (FeO₄²⁻) having a concentration of 1-100 mmol/l and one or more transition metal oxyanions selected from the group consisting of permanganate, molybdate, vanadate, tungstate and combinations thereof and wherein the solution has a pH between 13 and 13.5.

[0029] Conveniently the ferrate (VI) is selected from a sodium ferrate (VI) salt, a potassium ferrate (VI) salt, a solution of ferrate (VI) in potassium hydroxide, a solution of ferrate (VI) in sodium hydroxide and mixtures thereof.

[0030] Advantageously the metal surface is selected from aluminium, aluminium alloy, steel or other ferrous metals.

[0031] Preferably the solution further comprises a salt selected from an alkali metal, or an alkaline earth metal, nitrate, chloride, fluoride or combinations thereof.

[0032] Conveniently the metal surfaces contacted with the oxidising solution for between 1 second and 5 minutes.

[0033] Advantageously the ferrate solution has a transition metal oxyanion concentration between 0.1% and 5% by weight.

[0034] Preferably the aqueous oxyanion solution further comprises one or more additional oxidising agents selected from peroxide, hypochlorite, ozone and combinations thereof.

[0035] Conveniently the aqueous solution further comprises ethylenediaminetetraacetic acid.

[0036] The method may additionally comprise the step of contacting the oxidised metal surface with a post treatment solution containing one or more compounds selected from an alkali metal silicate, an alkali metal borate, an alkali metal phosphate or mixtures thereof to
provide an oxide film conversion coating.

[0037] The method may further comprise contacting the oxide film conversion coating with lithium nitrate.

[0038] The method may additionally comprise contacting the oxide film conversion coating with calcium hydroxide.

[0039] Optionally the method may further comprise the steps of cleaning the metal surface prior to contacting the metal surface with ferrate solution and/or exposing the cleaned metal surface to boiling water or anodisation to form an oxide or hydrous oxide layer.

[0040] It is also optional to contact the conversion coating surface formed by ferrate oxidation with a post treatment solution containing one or more compounds selected from an alkali metal silicate, an alkali metal borate, an alkali metal phosphate, lithium nitrate, magnesium hydroxide, calcium hydroxide, barium hydroxide or mixtures thereof. Preferably, the concentration of the one or more compounds is between about 0.015% and about 5% by weight. If calcium hydroxide is used, the preferred concentration is between about 0.06% and about 0.09% by weight and, preferably, the solution is prepared in water in the absence of carbon dioxide. The post treatment is preferably conducted at a solution temperature between about 10°C and about 100°C for a period of between about 1 minute and about 20 minutes.

BRIEF DESCRIPTION OF THE DRAWINGS

[0041] So that the above recited features and advantages of the present invention can be understood in detail, a more particular description of the invention, briefly summarised above, may be had by reference to the embodiments thereof which are illustrated in the appended drawings. It is to be noted, however, that the appended drawings illustrate only typical embodiments of this invention and are therefore not to be considered limiting of its scope, for the invention may admit to other equally effective embodiments.

[0042] Figure 1 is a graph showing salt fog survival of conversion coatings prepared with at two ferrate concentrations without oxanions, with molybdate, with permanganate, and with both molybdate and permanganate.

[0043] Figure 2 is a table showing salt fog survival of ferrate conversion coatings prepared from various ferrate solutions with and without pre-treatment steps or post-sealing steps.

DETAILED DESCRIPTION OF THE INVENTION

[0044] The present invention provides a conversion coating process that forms a stable and corrosion-resistant oxide film on the surface of metal substrates using ferrate (V1) as the oxidising agent. The conversion coating process uses an aqueous solution comprising ferrate anions, preferably having a ferrate anion concentration between 1 millimolar (about 0.0166% by weight) and 100 millimolar (about 1.66% by weight). The solution also includes one or more transition metal oxanions that form stable metal oxides in the coatings and act as inhibitors to corrosion of the coated metal. The transition metal oxanions are selected from permanganate, molybdate, vanadate, tungstate, or combinations thereof, preferably at a concentration between about 0.1% and about 5% by weight. The coating process is carried out at temperatures ranging between 25°C and 100°C, and a contact time ranging between 1 second and 5 minutes. The conversion coating may be produced on various metal surfaces or substrates, including but not limited to aluminium, aluminium alloys, steels (e.g. carbon steels and stainless steels), and other ferrous metals. The pH of the ferrate solution is 13-13.5 or greater than 13.5.

[0045] Optionally, yet preferably, the surface of the metal substrate is pre-treated before being contacted with the aqueous ferrate solution. Most preferably, the metal surface is cleaned by sonicating in acetone for 30 minutes, then cleaned in an alkaline solution. The cleaned metal surface may then be immersed in a deoxidising solution such as LNC deoxidiser (Oakite Products Inc., Berkeley Heights, New Jersey) to remove any residual oxide film from the metal surface. If the metal is aluminium or an aluminium alloy, the cleaned surface may then be exposed to boiling water or anodisation to form an oxide layer.

[0046] Furthermore, the invention may include an optional post-treatment process for the conversion coating. After the metal surface has been oxidised with a ferrate-containing conversion coating solution, the conversion coating can then be sealed with a post-treatment solution containing a sealant selected from an alkali metal silicate, an alkali metal borate, an alkali metal phosphate, lithium nitrate, magnesium hydroxide, calcium hydroxide, or barium hydroxide, with the most preferred sealant being calcium hydroxide. The preferred conditions for the post-treatment include a sealant concentration between about 0.015% and about 5% by weight, a solution temperature between about 10°C to about 100°C, and a contact time between about 1 minute and about 20 minutes. If calcium hydroxide is used, the post-treatment solution most preferably contains between about 0.06% and about 0.09% by weight calcium hydroxide and is prepared with water having a reduced carbon dioxide concentration.

[0047] The post-treatment step, for example using calcium hydroxide, is performed by reducing the concentration of carbon dioxide in water, forming a solution by combining calcium hydroxide with the water having a reduced concentration of carbon dioxide, and providing contact between the metal surface and the solution. The concentration of carbon dioxide in water may be reduced through any known process, but is preferably reduced by heating the water, most preferably to a temperature between 50°C and 100°C. Other processes for reducing the carbon dioxide concentration in water include passing the water through an electroosmotic...
metal salt concentration is between about 0.1% and lithium chloride, and sodium nitrate. The preferred alkali trates, chlorides and fluorides, preferably lithium nitrate, line earth metal salts include but are not limited to ni-
sion coating reaction. Suitable alkaline earth metal salts or anions or salts. 

Example 1. Preparation of aluminium or aluminium alloy panels (Comparative Example) 

Example 2. Aluminium or aluminium alloy panels treated with conversion coating solutions containing ferrate (VI) in combination with one or more oxyanions or salts.

Example 3. Aluminium or aluminium alloy panels treated with conversion coating solutions containing ferrate (VI) and EDTA at low hydroxide concentrations in combination with one or more oxyanions or salts.
or more of potassium permanganate and potassium molybdate, and 0.5% to 1.0% of one or more of lithium chloride, lithium nitrate, of sodium nitrate. Aluminium panels prepare as described in Example 1, were immersed in this conversion coating solutions for between 1 second and 10 minutes at temperatures between 25°C and 80°C. The panels were then rinsed thoroughly with deionised water, dried in air for 48 to 94 hours, and tested by salt fog spray according to the ASTM B-117 test method (samples were placed at 15° angle).

Example 4. Aluminium or aluminium alloy panels treated with conversion coating solutions containing only ferrate (VI) and then treated with post-sealants. (Comparative Example)

[0057] Aqueous solutions of ferrate (VI) having concentrations ranging between 3 - 80 mmol/l ferrate (VI) were prepared. Aluminium panels, prepared as described in Example 1, were immersed in each of the solutions for periods ranging from 1 second to 5 minutes at a temperature ranging between 25°C and 80°C. The treated aluminium panels then received post-treatment by being immersed, first in an aqueous solution containing 0.09% by weight calcium hydroxide and 0.6% by weight lithium nitrate at 100°C for 20 minutes, and second in an aqueous solution containing 2.4% by weight alkali metal silicate at 80°C for 2 minutes. The panels were then rinsed thoroughly with deionised water, dried in air for 48 to 94 hours, and tested by salt fog spray according to the ASTM B-117 test method (samples were placed at 15° angle).

Example 5. Aluminium or aluminium alloy panels treated with conversion coating solutions containing ferrate (VI) in combination with one or more additional oxidising agents selected from the group consisting of permanganate, molybdate, vanadate, tungstate and combinations thereof and wherein the solution has a pH between 13 and 13.5.

[0058] Aqueous solutions of ferrate (VI) having concentrations between 3.10 mmol/l ferrate (VI), with or without 0.5% sodium nitrate, 1.0% to 3.0% of one or more of potassium permanganate and potassium molybdate, and 0.5% to 1.0% of one or more of lithium chloride, lithium nitrate, of sodium nitrate were prepared. The aluminium panels prepared as described in Example 1, were immersed in this conversion coating solution for between 1 second and 5 minutes at temperatures between 25°C and 80°C. The treated aluminium panels then received post-treatment by being immersed, first in an aqueous solution containing 0.09% by weight calcium hydroxide and 0.6% by weight lithium nitrate at 100°C for 20 minutes, and second in an aqueous solution containing 2.4% by weight alkali metal silicate at 80°C for 2 minutes. The panels were then rinsed thoroughly with deionised water, dried in air for 48 to 94 hours, and tested by salt fog spray according to the ASTM B-117 test method (samples were placed at 15° angle).

Example 6. Aluminium or aluminium alloy panels treated with conversion coating solutions containing ferrate (VI) and EDTA at low hydroxide concentrations in combination with one or more anions or salts and then treated with post-sealants.

[0059] Aqueous solutions of ferrate (VI) with EDTA having concentrations between 0.0166% to 1.66% ferrate (VI) at pH between 13 and 13.5 were prepared. The solutions could also contained 1.0% to 3.0% of one or more of potassium permanganate and potassium molybdate, and 0.5% to 1.0% of one or more of lithium chloride, lithium nitrate, of sodium nitrate. Aluminium panels prepared as described in Example 1, were immersed in this conversion coating solutions for between 1 second to 5 minutes at temperatures between 25°C and 80°C. The treated aluminium panels were then immersed in one or more post-treatment solutions, such as alkali metal silicate and calcium hydroxide, between 80°C and 100°C for 1 minute to 20 minutes. The panels were then rinsed thoroughly with deionised water, dried in air for 48 to 94 hours, and tested by salt fog spray according to the ASTM B-117 test method (samples were placed at 15° angle).

Example 7. Stabilisation of ferrate (VI) in the conversion coating solution

[0060] The ferrate (VI) anions in the conversion coating solution may be stabilised by the addition of oxidisers such as peroxides, hypochlorites, ozone, or other oxidisers. The concentrations of these oxidisers can be varied between 0.1% and 0.5% by weight.

Claims

1. A solution for forming a conversion coating on a metal surface, the solution comprising ferrate (V1) (FeO₄²⁻) anions having a concentration of 1-100 mmol/l and one or more transition metal oxoanions selected from the group consisting of permanganate, molybdate, vanadate, tungstate and combinations thereof and wherein the solution has a pH greater than 13.5.

2. A solution for forming a conversion coating on a metal surface, the solution comprising ferrate (V1) (FeO₄²⁻) anions having a concentration of 1-100 mmol/l and one or more transition metal oxoanions selected from the group consisting of permanganate, molybdate, vanadate, tungstate and combinations thereof and wherein the solution has a pH between 13 and 13.5.

3. The solution of Claim 1 or 2 further comprising one or more additional oxidising agents selected from
the group consisting of peroxide, hypochlorite, ozone and combinations thereof.

4. The solution of Claim 1, 2 or 3 wherein the ferrate (VI) oxyanion is provided by a compound selected from a sodium ferrate (VI) salt, a potassium ferrate (VI) salt, a solution of ferrate (VI) in potassium hydroxide, a solution of ferrate (VI) in sodium hydroxide and mixtures thereof.

5. The solution of any one of Claims 1 to 4 further comprising ethylenediaminetetraacetic acid.

6. The solution of any one of Claims 1 to 5 further comprising a salt selected from an alkali metal, or an alkaline earth metal, nitrate, chloride, fluoride or combinations thereof.

7. A method for treating a metal surface, comprising cleaning and deoxidising the metal surface, rinsing the deoxidised and rinsing metal surface with an aqueous oxidising solution at a temperature in the range of 25-100 °C, allowing the metal surface to be oxidised by the oxidising solution, and removing the oxidised metal surface from being in contact with the solution, characterised in that the oxidising solution is an aqueous solution comprising ferrate (VI) (FeO₄²⁻) having a concentration of 1-100 mmol/l and one or more transition metal oxyanions selected from the group consisting of permanganate, molybdate, vanadate, tungstate and, combinations thereof and wherein the solution has a pH greater than 13.5.

8. A method for treating a metal surface, comprising cleaning and deoxidising the metal surface, rinsing the deoxidised and rinsing metal surface with an aqueous oxidising solution at a temperature in the range of 25-100 °C, allowing the metal surface to be oxidised by the oxidising solution, and removing the oxidised metal surface from being in contact with the solution, characterised in that the oxidising solution is an aqueous solution comprising ferrate (VI) (FeO₄²⁻) having a concentration of 1-100 mmol/l and one or more transition metal oxyanions selected from the group consisting of permanganate, molybdate, vanadate, tungstate and, combinations thereof and wherein the solution has a pH between 13 and 13.5.

9. The method of Claim 7 or 8 wherein the ferrate (VI) is selected from a sodium ferrate (VI) salt, a potassium ferrate (VI) salt, a solution of ferrate (VI) in potassium hydroxide, a solution of ferrate (VI) in sodium hydroxide and mixtures thereof.

10. The method of Claim 7, 8 or 9 wherein the metal surface is selected from aluminium, aluminium alloy, steel or other ferrous metals.

11. The method of any one of Claims 7 to 10 wherein the solution further comprises a salt selected from an alkali metal, or an alkaline earth metal, nitrate, chloride, fluoride or combinations thereof.

12. The method of any one of Claims 7 to 11 wherein the metal surfaces are contacted with the oxidising solution for between 1 second and 5 minutes.

13. The method of any one of Claims 7 to 12 wherein the ferrate solution has a transition metal oxyanion concentration between 0.1% and 5% by weight.

14. A method of any one of Claims 7 to 13 wherein the aqueous oxyanion solution further comprises one or more additional oxidising agents selected from peroxide, hypochlorite, ozone and combinations thereof.

15. The method of any one of Claims 7 to 14 wherein the aqueous solution further comprises ethylenediaminetetraacetic acid.

16. The method of any one of Claims 7 to 15 comprising the step of contacting the oxidised metal surface with a post treatment solution containing one or more compounds selected from an alkaline metal silicate, an alkali metal borate, an alkali metal phosphate or mixtures thereof to provide an oxide film conversion coating.

17. The method of Claim 16 further comprising contacting the oxidised metal surface conversion coating with lithium nitrate.

18. The method of Claim 16 or 17 further comprising contacting the oxide film conversion coating with calcium hydroxide.

Patentansprüche

1. Lösung zur Ausbildung einer Konversionschicht auf einer Metalloberfläche, wobei die Lösung Ferrate(VI) (FeO₄²⁻)-Anionen mit einer Konzentration von 1 - 100 mmol/l und ein oder mehrere Übergangsmetall-Oxyanionen, die ausgewählt sind aus der Gruppe, bestehend aus Permanganat, Molybdät, Vanadat, Wolframat und Kombinationen derselben, umfaßt und wobei die Lösung einen pH von mehr als 13,5 aufweist.

2. Lösung zur Ausbildung einer Konversionschicht auf einer Metalloberfläche, wobei die Lösung Ferrate(VI)
Verfahren zur Behandlung einer Metalloberfläche, wobei die Metalloberfläche in Kontakt mit der Lösung und die oxidierte Metalloberfläche in einigen Fällen in wäßriger Lösung weiter ein oder mehrere zusätzliche Oxidationsmittel umfaßt, die ausgewählt sind aus der Gruppe, bestehend aus Permanganat, Molybdät, Vanadat, Wolframat und Kombinationen derselben, umfaßt und wobei die Lösung einen pH zwischen 13 und 13,5 aufweist.

3. Lösung nach Anspruch 1 oder 2, **dadurch gekennzeichnet, daß** sie weiter ein oder mehrere zusätzliche Oxidationsmittel umfaßt, die ausgewählt sind aus der Gruppe, bestehend aus Peroxid, Hypochlorit, Ozon und Kombination derselben.

4. Lösung nach Anspruch 1, 2 oder 3, **dadurch gekennzeichnet, daß** das Ferrat(VI)-Oxionen bereitgestellt wird durch eine Verbindung, die ausgewählt ist aus einem Natriumferrat(VI)-Salz, einem Kaliumferrat(VI)-Salz, einer Lösung von Ferrat(VI) in Kaliumhydroxid, einer Lösung von Ferrat(VI) in Natriumhydroxid und Mischungen derselben.

5. Lösung nach einem der Ansprüche 1 bis 4, **dadurch gekennzeichnet, daß** sie weiter Ethylenamin-tetraessigsäure umfaßt.

6. Lösung nach einem der Ansprüche 1 bis 5, **dadurch gekennzeichnet, daß** sie weiter ein Salz umfaßt, das ausgewählt ist aus einem Alkalimetall- oder einem Erdalkalimetallnitrat, -chlorid, -fluorid oder Kombinationen derselben.

7. Verfahren zur Behandlung einer Metalloberfläche, welches Säubern und Desoxidieren der Metalloberfläche, Spülen der desoxidierten Metalloberfläche mit Wasser, Inkontaktbringen der desoxidierten und gespülten Metalloberfläche mit einer wäßrigen oxidierenden Lösung bei einer Temperatur im Bereich von 25 bis 100°C, Zulassen, daß die Metalloberfläche durch die oxidierende Lösung oxidiert wird, und Entfernen der oxidierten Metalloberfläche aus dem Kontakt mit der Lösung umfaßt, **dadurch gekennzeichnet, daß** die oxidierende Lösung eine wäßrige Lösung ist, die Ferrat(VI) (FeO$_4^{2-}$) mit einer Konzentration von 1 bis 100 mmol/l und ein oder mehrere Übergangsmetall-Oxionen, die ausgewählt sind aus der Gruppe, bestehend aus Permanganat, Molybdät, Vanadat, Wolframat und Kombination derselben, umfaßt, und wobei die Lösung einen pH von mehr als 13,5 aufweist.

8. Verfahren zur Behandlung einer Metalloberfläche, welches Säubern und Desoxidieren der Metalloberfläche, Spülen der desoxidierten Metalloberfläche mit Wasser, Inkontaktbringen der desoxidierten und gespülten Metalloberfläche mit einer wäßrigen oxidierenden Lösung bei einer Temperatur im Bereich von 25 bis 100°C, Zulassen, daß die Metalloberflä-

5 che durch die oxidierende Lösung oxidiert wird, und Entfernen der oxidierten Metalloberfläche aus dem Kontakt mit der Lösung umfaßt, **dadurch gekennzeichnet, daß** die oxidierende Lösung eine wäßrige Lösung ist, die Ferrat(VI) (FeO$_4^{2-}$) mit einer Konzentration von 1 bis 100 mmol/l und ein oder mehrere Übergangsmetall-Oxionen, die ausgewählt sind aus der Gruppe, bestehend aus Permanganat, Molybdät, Vanadat, Wolframat und Kombination derselben, umfaßt, und wobei die Lösung einen pH zwischen 13 und 13,5 aufweist.

9. Verfahren nach Anspruch 7 oder 8, **dadurch gekennzeichnet, daß** das Ferrat(VI) ausgewählt wird aus einem Natriumferrat(VI)-Salz, einem Kaliumferrat(VI)-Salz, einer Lösung von Ferrat(VI) in Kaliumhydroxid, einer Lösung von Ferrat(VI) in Natriumhydroxid und Mischungen derselben.

10. Verfahren nach Anspruch 7, 8 oder 9, **dadurch gekennzeichnet, daß** die Metalloberfläche ausge wählt wird aus Aluminium, Aluminiumlegierung, Stahl oder anderen Eisenmetallen.

11. Verfahren nach einem der Ansprüche 7 bis 10, **dadurch gekennzeichnet, daß** die Lösung weiter ein Salz umfaßt, das ausgewählt ist aus einem Alkalimetall- oder einem Erdalkalimetallnitrat, -chlorid, -fluorid oder Kombinationen derselben.

12. Verfahren nach einem der Ansprüche 7 bis 11, **dadurch gekennzeichnet, daß** die Metalloberflächen mit der oxidierenden Lösung für zwischen 1 Sekunde und 5 Minuten in Kontakt gebracht werden.

13. Verfahren nach einem der Ansprüche 7 bis 12, **dadurch gekennzeichnet, daß** die Ferrat-Lösung eine Übergangsmetall-Oxionen-Konzentration zwischen 0,1 und 5 Gew.-% aufweist.

14. Verfahren nach einem der Ansprüche 7 bis 13, **dadurch gekennzeichnet, daß** die wäßrige Oxionen-Lösung weiter ein oder mehrere zusätzliche Oxidationsmittel umfaßt, die ausgewählt sind aus Peroxid, Hypochlorit, Ozon und Kombinationen derselben.

15. Verfahren nach einem der Ansprüche 7 bis 14, **dadurch gekennzeichnet, daß** die wäßrige Lösung weiter Ethylenamintetraessigsäure umfaßt.

16. Verfahren nach einem der Ansprüche 7 bis 15, **dadurch gekennzeichnet, daß** es den Schritt umfaßt, daß die oxidierte Metalloberfläche mit einer Nachbehandlungslösung in Kontakt gebracht wird, die ein oder mehrere Verbindungen enthält, die ausgewählt sind aus einem Alkalimetallsilikat, einem Alkalimetallborat, einem Alkalimetallphosphat oder
Mischungen derselben, um eine Oxidfilm-Konversionschicht bereitzustellen.

17. Verfahren nach Anspruch 16, dadurch gekennzeichnet, daß es weiter umfaßt, daß die Oxidfilm-Konversionschicht mit Lithiumnitrat in Kontakt gebracht wird.

18. Verfahren nach Anspruch 16 oder 17, dadurch gekennzeichnet, daß es weiter umfaßt, daß die Oxidfilm-Konversionschicht mit Calciumhydroxid in Kontakt gebracht wird.

Revendications

1. Solution pour former un revêtement de conversion sur une surface métallique, la solution comprenant des anions ferrate (VI) (FeO₄²⁻) ayant une concentration de 1 à 100 mmol/l et un ou plusieurs oxyanions de métal de transition choisis dans le groupe constitué par le permanganate, le molybdate, le vanadate, le tunstate et les combinaisons de ceux-ci et où la solution a un pH supérieur à 13,5.

2. Solution pour former un revêtement de conversion sur une surface métallique, la solution comprenant des anions ferrate (VI) (FeO₄²⁻) ayant une concentration de 1 à 100 mmol/l et un ou plusieurs oxyanions de métal de transition choisis dans le groupe constitué par le permanganate, le molybdate, le vanadate, le tunstate et les combinaisons de ceux-ci et où la solution a un pH compris entre 13 et 13,5.

3. Solution selon la revendication 1 ou 2, comprenant en outre un ou plusieurs agents oxydants supplémentaires choisis dans le groupe constitué par un peroxyde, un hypochlorite, l'oxygene et les combinaisons de ceux-ci.

4. Solution selon la revendication 1, 2 ou 3, dans laquelle l'oxyanion ferrate (VI) est fourni par un composé choisi parmi un sel ferrate (VI) de sodium, un sel ferrate (VI) de potassium, une solution de ferrate (VI) dans de l'hydroxyde de potassium, une solution de ferrate (VI) dans de l'hydroxyde de sodium et les mélanges de ceux-ci.

5. Solution selon l'une quelconque des revendications 1 à 4, comprenant en outre de l'acide éthylènediamine-tétracétique.

6. Solution selon l'une quelconque des revendications 1 à 5, comprenant en outre un sel choisi parmi un nitrate, un chlorure, un fluorure de métal alcalin ou de métal alcalino-terreux, ou des combinaisons de ceux-ci.

7. Procédé de traitement d'une surface métallique, comprenant le nettoyage et la désoxydation de la surface métallique, le rinçage de la surface métallique désoxydée avec de l'eau, la mise en contact de la surface métallique désoxydée et rincée avec une solution aqueuse oxydante à une température dans la gamme de 25 à 100 °C, le fait de laisser la surface métallique être oxydée par la solution oxydante, et le retrait de la surface métallique oxydée en contact avec la solution, caractérisé en ce que la solution oxydante est une solution aqueuse comprenant des anions ferrate (VI) (FeO₄²⁻) ayant une concentration de 1 à 100 mmol/l et un ou plusieurs oxyanions de métal de transition choisis dans le groupe constitué par le permanganate, le molybdate, le vanadate, le tunstate et les combinaisons de ceux-ci et où la solution a un pH supérieur à 13,5.

8. Procédé de traitement d'une surface métallique, comprenant le nettoyage et la désoxydation de la surface métallique, le rinçage de la surface métallique désoxydée avec de l'eau, la mise en contact de la surface métallique désoxydée et rincée avec une solution aqueuse oxydante à une température dans la gamme de 25 à 100 °C, le fait de laisser la surface métallique être oxydée par la solution oxydante, et le retrait de la surface métallique oxydée en contact avec la solution, caractérisé en ce que la solution oxydante est une solution aqueuse comprenant des anions ferrate (VI) (FeO₄²⁻) ayant une concentration de 1 à 100 mmol/l et un ou plusieurs oxyanions de métal de transition choisis dans le groupe constitué par le permanganate, le molybdate, le vanadate, le tunstate et les combinaisons de ceux-ci et où la solution a un pH compris entre 13 et 13,5.

9. Procédé selon la revendication 7 ou 8, dans lequel le ferrate (VI) est choisi parmi un sel ferrate (VI) de sodium, un sel ferrate (VI) de potassium, une solution de ferrate (VI) dans de l'hydroxyde de potassium, une solution de ferrate (VI) dans de l'hydroxyde de sodium et les mélanges de ceux-ci.

10. Procédé selon la revendication 7, 8 ou 9, dans lequel la surface métallique est choisie parmi l'aluminium, un alliage d'aluminium, l'acier ou d'autres métaux ferreux.

11. Procédé selon l'une quelconque des revendications 7 à 10, dans lequel la solution comprend en outre un sel choisi parmi un nitrate, un chlorure, un fluorure de métal alcalin ou de métal alcalino-terreux, ou des combinaisons de ceux-ci.

12. Procédé selon l'une quelconque des revendications 7 à 11, dans lequel les surfaces métalliques sont mises en contact avec la solution oxydante pendant
une durée comprise entre 1 seconde et 5 minutes.

13. Procédé selon l'une quelconque des revendications 7 à 12, dans lequel la solution de ferrate a une concentration en oxyanion de métal de transition comprise entre 0,1 % et 5 % en poids.

14. Procédé selon l'une quelconque des revendications 7 à 13, dans lequel la solution aqueuse d'oxyanion comprend en outre un ou plusieurs agents oxydants supplémentaires choisis parmi un peroxyde, un hypochlorite, l'ozone et les combinaisons de ceux-ci.

15. Procédé selon l'une quelconque des revendications 7 à 14, dans lequel la solution aqueuse comprend en outre de l'acide éthylénediaminetétracétique.

16. Procédé selon l'une quelconque des revendications 7 à 15, dans lequel l'étape de mise en contact de la surface métallique oxydée avec une solution de post-traitement contenant un ou plusieurs composés choisis parmi un silicate de métal alcalin, un borate de métal alcalin, un phosphate de métal alcalin, ou des mélanges de ceux-ci, pour fournir un revêtement de conversion d'un film d'oxyde.

17. Procédé selon la revendication 16, comprenant en outre la mise en contact du revêtement de conversion d'un film d'oxyde avec du nitrate de lithium.

18. Procédé selon la revendication 16 ou 17, comprenant en outre la mise en contact du revêtement de conversion d'un film d'oxyde avec de l'hydroxyde de calcium.
FIG. 1
<table>
<thead>
<tr>
<th>Corresponding Example</th>
<th>Boehmite</th>
<th>Conversion Solution Conditions</th>
<th>Post-Sealants</th>
<th>Corrosion Performance</th>
</tr>
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<tbody>
<tr>
<td></td>
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<td>Ferrate (mM)</td>
<td>pH</td>
<td>Additives</td>
</tr>
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<td>14</td>
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<td>Conversion Solution Conditions</td>
<td>Post-Sealants</td>
<td>Corrosion Performance</td>
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* Comparative Example
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<tr>
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<td>10 12* 1.5%KMnO₄, 1.5%K₂MoO₄, 1%NaNO₃</td>
<td>80 2 min</td>
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<tr>
<td>s</td>
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<td>80 2 min</td>
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</tbody>
</table>

* Comparative Example