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(54) **METHOD OF MAKING ALUMINUM-COATED METAL**

(57) A method of coating a metal substrate (12) is disclosed in which the metal substrate is disposed as an anode in an electrolytic circuit with an aqueous alkaline liquid electrolyte. An electrical voltage differential is applied to the metal substrate and a cathode. The treated

metal substrate is disposed as a cathode in an electrolytic circuit with an ionic liquid electrolyte and an aluminum salt. An electrical voltage differential is applied to the metal substrate and an anode to form an aluminum layer (14) on the metal substrate.

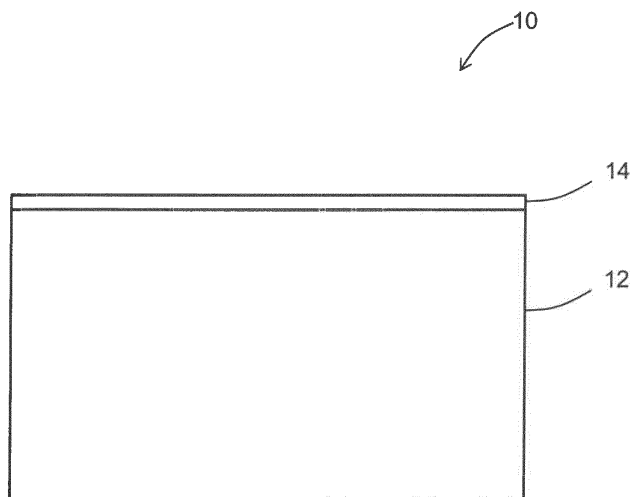


FIG. 1

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Description

[0001] This invention was made with Government support under contract number W911W6-12-2-0003 awarded by the United States Army. The Government has certain rights in the invention.

BACKGROUND

[0002] Metal plating such as cadmium plating has been widely used on various materials, including but not limited to high-strength steel, aircraft components, fasteners, electrical connectors, and numerous others. Metal plating can be used to promote properties such as corrosion resistance, lubricity, and electrical conductivity. Cadmium has been used as a metal plating material for various reasons such as the cost of plating and its anti-galling performance (no adhesive wear on threaded surfaces). However, continued commercial uses of cadmium have been facing pressure due to health concerns in recent years, including being listed as a substance of very high concern (SVHC) in 2012 by the European Union environment & safety regulatory agency REACH.

[0003] Various metal plating technologies have been developed and evaluated over the years. For example, aluminum has been proposed as a metal plating material, and has been approved for corrosion protection of high-strength structural steels in aircraft as set forth in specifications such as MIL-DTL-83488. However, various technical issues continue to present challenges. Commercially available aluminum metal plating processes utilize toxic or environmentally unfriendly organic solvents and pyrophoric alkylaluminum compounds that require extra measures for operation under inert conditions. Therefore, there continues to be a need for further developments regarding aluminum metal coatings.

[0004] High strength steels (HSS) are used throughout aerospace industries for components such as aircraft landing gear, bolts, aircraft tail hooks on aircraft carriers etc. High strength steels are protected by sacrificial coatings such as electroplated cadmium, zinc-nickel and non-electrolytic aluminum-based SermeTel (Praxair Surface Technologies) coatings. It has been known that HSS are prone to hydrogen embrittlement representing brittle mechanical failures under stress that is manifested by brittle intergranular fracture and trans-granular cleavage. Incorporation of hydrogen during either the electroplating process or the corrosion during service promotes the increased risk of failure arising from hydrogen embrittlement. Porous electroplated coatings can allow hydrogen to be released from the steel substrates via a post-plating baking process. However, substrates coated with porous coatings can become susceptible to re-embrittlement due to galvanic cells formed on exposed area. Dense coatings of lower porosity can mitigate the risk of hydrogen re-embrittlement; however, dense coatings can prevent hydrogen from being released. Hydrogen embrittlement can also be caused by pre-treatment processes for

of HSS, such as treatment with acids or electrolytic cathodic cleaning which can generate hydrogen.

BRIEF DESCRIPTION

[0005] According to some embodiments, a method of coating a metal substrate comprises disposing the metal substrate as an anode in an electrolytic circuit comprising an aqueous alkaline liquid electrolyte. An electrical voltage differential is applied to the metal substrate and a cathode. The treated metal substrate is disposed as a cathode in an electrolytic circuit comprising a liquid electrolyte that comprises an ionic liquid and an aluminum salt. An electrical voltage differential is applied to the metal substrate and an anode to form a layer comprising aluminum on the metal substrate.

[0006] According to some embodiments, an article comprises a metal substrate and a layer thereon comprising aluminum. The layer comprising aluminum has a volumetric density greater than 99%, and the coated article meets or exceeds hydrogen embrittlement test requirements of ASTM F519-10.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] Subject matter of this disclosure is particularly pointed out and distinctly claimed in the claims at the conclusion of the specification. The foregoing and other features, and advantages of the present disclosure are apparent from the following detailed description taken in conjunction with the accompanying drawings in which:

FIG. 1 is a schematic depiction of a cross-sectional view of a coated article as described herein;

FIG. 2 is a schematic depiction of an example embodiment of a method as described herein; and

FIG. 3 is a schematic depiction of another example embodiment of a method as described herein.

DETAILED DESCRIPTION

[0008] With reference now to the Figures, FIG. 1 schematically depicts a cross-sectional view of a coated article 10 comprising a substrate 12 having thereon a surface layer 14 comprising aluminum. The substrate 12 can comprise high strength steels that are particularly prone to hydrogen embrittlement due to lack of corrosion resistance and facile hydrogen diffusion in the steel lattice. Further, the substrate 12 comprises a metal or metal alloy having a first oxidation-reduction equilibrium (corrosion) potential more noble than aluminum and aluminum alloys. This difference in potential can allow the layer to provide sacrificial corrosion protection in an electrolyte that is experienced in the service environment where the parts are used. In some embodiments, the metal or metal alloy of substrate 12 has an electrode potential of -1.0 V

to 0 V with respect to saturated calomel electrode (SCE) in 3.5% wt. sodium chloride solution or sea water solution or synthetic sea water solution, more specifically -0.6 to -0.1, and even more specifically from -0.4 V to -0.2 V. Examples of metals or metal alloys for the substrate 12 include but are not limited to high-strength steels (e.g., D6AC, 300M, M-50, AERMET 100, 4330, 4340, 52100). In some embodiments, the substrate 12 comprises a high strength low alloy (HSLA) steel as that term is defined by SAE (Society of Automotive Engineers) standards.

[0009] The thickness of layer 14 can be specified to meet target specifications. In some embodiments, the layer 14 has a thickness in a range having a low end of 2.5 μm (0.0001 inches), more specifically 7.5 μm (0.0003 inches), and even more specifically 12.5 μm (0.0005 inches), and an upper end of 17.5 μm (0.0007 inches), more specifically 25 μm (0.001 inches), and even more specifically 250 μm (0.010 inches). The above range endpoints can be independently combined to serve as a disclosure of a number of different ranges, which are hereby expressly disclosed. In some embodiments, the layer 14 can be utilized to promote resistance to corrosion. In some embodiments, the layer 14 can be utilized to promote resistance to galling along contact portions of the article. In some embodiments, the layer 14 can be disposed on surface to be subjected to sliding contact with another article or component. Such articles can include, but are not limited to, threaded fasteners, press-fit connections, propeller barrels, electrical connectors, press-fit high strength steel bolts used in turboprop propellers, and other various fasteners or connectors.

[0010] In some example embodiments, articles such as shown in FIG. 1 can be prepared by methods shown in FIGS. 2 and 3. In some embodiments, the surface of the substrate 12 can optionally be subjected to physical surface preparation such as degreasing, grit blasting, or both degreasing and grit blasting as shown in FIGS. 2 and 3. Examples of degreasing agents include organic solvents such as acetone or methyl ethyl ketone, alkaline degreasers such as aqueous solutions of sodium hydroxide, potassium hydroxide, or ammonia, or aqueous surfactants with degreasing capability. After degreasing, the substrate can optionally be dried such as by radiant heat or blowing with air. Grit blasting can be performed by directing abrasive particles at the substrate at velocities of 50 to 100 in/min. Examples of materials for grit blasting include alumina grit, silicon carbide grit, steel grit, or glass particles. The particles for grit blasting can have particle sizes expressed as mean diameter and distribution as described in ANSI B74.12-2001.

[0011] As further shown in FIGS. 2 and 3, after optional degreasing and grit blasting, the substrate is subjected to anodic alkaline electrolytic treatment. This treatment involves disposing the metal substrate as an anode in an electrolytic circuit comprising an aqueous alkaline liquid electrolyte, and applying an electrical voltage differential between the metal substrate anode and a cathode. Conditions for anodic alkaline electrolytic treatment can be

controlled to promote formation of oxygen at the metal substrate surface according to the reaction $4\text{OH}^- \rightarrow 2\text{H}_2\text{O} + \text{O}_2$ and to minimize formation of metal oxide at the metal surface substrate. In some embodiments, the formation of oxygen at the metal substrate surface can promote cleaning of the metal substrate surface. The alkaline electrolyte can comprise aqueous solutions of alkaline compounds such as sodium hydroxide, potassium hydroxide, and their weak acid salts such as Na_2CO_3 , Na_3PO_4 , Na_2SiO_4 at concentrations in a range having a lower end of 15 wt.%, 10 wt.%, or 5 wt.%, and an upper end of 50 wt.%, 75 wt.%, or 100 wt.%. Commercial alkaline cleaning products such as Henkel Turco 4181 can be used as well. The above range endpoints can be independently combined to serve as a disclosure of a number of different ranges, each of which is hereby expressly disclosed. The alkaline electrolyte can have a pH in a range having a lower end of 9, 8, or 7.5, and an upper end of 14. The above range endpoints can be independently combined to serve as a disclosure of a number of different ranges, each of which is hereby expressly disclosed. The alkaline electrolyte can be at a temperature in a range having a lower end of 25°C and an upper end of 50°C. In some embodiments, the voltage differential applied between the cathode and the metal substrate anode can provide an electrical current density (based on anode surface area) between the cathode and anode in a range having a lower end of 5 mA/cm², 10 mA/cm², or 15 mA/cm², and an upper end of 25 mA/cm², 50 mA/cm², or 75 mA/cm², and can be applied for a duration in a range having a lower end of 15 seconds, 30 seconds, or 60 seconds, and an upper end of 120 seconds, 180 seconds, or 300 seconds. The above range endpoints can be independently combined to serve as a disclosure of a number of different ranges, each of which is hereby expressly disclosed. In some embodiments, the current can be pulsed or varied. Other conditions (e.g., temperature) can also be varied during anodic alkaline electrolytic treatment. After anodic alkaline electrolytic treatment, the metal substrate can be rinsed with deionized water and dried in nitrogen or air.

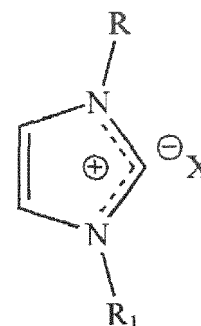
[0012] With reference now to FIG. 3, the anodic alkaline electrolytically-treated metal substrate can be further subjected to an anodic ionic liquid electrolytic treatment. This treatment involves disposing the metal substrate as an anode in an electrolytic circuit comprising a liquid electrolyte that comprises an ionic liquid, and applying an electrical voltage differential between the metal substrate anode and a cathode to induce current. In some embodiments, this treatment can etch the surface of the metal substrate, which can promote release of metal oxide from the surface. The ionic liquid electrolyte can be at a temperature in a range having a lower end of 25°C, 40°C, or 55°C, and an upper end of 60°C, 70°C, or 80°C. The above range endpoints can be independently combined to serve as a disclosure of a number of different ranges, each of which is hereby expressly disclosed. In some embodiments, the voltage differential applied between

the cathode and the metal substrate anode can be set to produce a current density (based on anode surface area) in a range having a lower end of 5 mA/cm², 10 mA/cm², or 15 mA/cm², and an upper end of 20 mA/cm², 30 mA/cm², or 40 mA/cm², and can be applied for a duration in a range having a lower end of 15 seconds, 30 seconds, or 45 seconds, and an upper end of 60 seconds, 120 seconds, or 300 seconds. The above range endpoints can be independently combined to serve as a disclosure of a number of different ranges, each of which is hereby expressly disclosed. In some embodiments, the voltage can be pulsed or varied. Other conditions (e.g., temperature) can also be varied during anodic ionic liquid electrolytic treatment. After anodic ionic liquid electrolytic treatment, the metal substrate can be rinsed (e.g., with methanol, ethanol, deionized water, or a combination of rinsing agents) and dried (e.g., with heat or blown air), or can remain in the ionic liquid electrolyte for further processing.

[0013] As further shown in FIG. 3, the anodic ionic liquid electrolytically-treated metal substrate can be subjected to sonicating treatment in the same or a different electrolyte bath. In some embodiments, anodic etching treatment of steel substrates in ionic liquids can produce smut on the substrate, which can interfere with the subsequent aluminum plating process, leading to poor coating quality. Sonicating the parts can be conducted in ionic liquids or in water-free organic solvents such as ethanol, toluene, acetone, etc. In some embodiments, sonic treatment can promote the removal of smut or other substances that may have been formed on the surface by the treatment process or are otherwise disposed on the surface. In some embodiments, sonicating treatment can involve exposure of the metal substrate to sonic energy in a frequency range having a lower end of 10 kHz and an upper end of 200 kHz. In some embodiments, the sonic treatment can be applied for a duration in a range having a lower end of 30 seconds and an upper end of 300 seconds. In some embodiments, the sonic energy can be pulsed or varied.

[0014] As further shown in FIGS. 2 and 3, a layer comprising aluminum can be deposited onto the treated metal substrate by disposing the metal substrate as a cathode in an electrolytic circuit comprising a liquid electrolyte that comprises an ionic liquid and an aluminum salt, and applying an electrical voltage differential between the metal substrate and an anode. As used herein, the term "ionic liquid" means a salt having a melting point below the processing temperature (e.g., below 100°C). In some embodiments, the ionic liquid is non-volatile or of low volatility at the process temperature. Cations for the ionic liquid used as electrolyte for cathodic electrodeposition of aluminum shown in FIGS. 2 and 3, as well as for the anodic electrolytic treatment shown in FIG. 3, can include, but are not limited to imidazolium (e.g., 1-ethyl-3-methylimidazolium, 1-ethyl-2,3-dimethylimidazolium, 1-butyl-3-methylimidazolium ("BMI"), 1-hexyl-3-methylimidazolium ("HMI"), pyridinium (e.g., N-methylpyridinium),

tetraalkylammonium, pyrrolidinium (e.g., 1-butyl-1-methyl-pyrrolidinium ("BMPyr")), trialkylsulfonium (e.g., triethylsulfonium), pyrazolium, triazolium, thiazolium, oxazolium, pyridazinium, pyrimidinium, pyrazinium. Exemplary anions for ionic liquids used in the embodiments described herein include, but are not limited to, chloroaluminate (Al₂Cl₇⁻), tetrafluoroborate (BF₄⁻), hexafluorophosphate (PF₆⁻), trifluoromethanesulfonate (CF₃SO₃⁻), bis(trifluoromethylsulfonyl)imide, trifluoroethanoate, nitrate, SCN⁻, HSO₄⁻, HCO₃⁻, CH₃SO₃⁻, CH₃CH₂SO₄⁻, (CH₃(CH₂)₃O)₂POO⁻, (CF₃SO₂)₂N⁻, dicyanamide, (CF₃CF₂SO₂)₂N⁻, L-(+)-lactate, CH₃SO₄⁻, and CH₃COO⁻, and the like. In some embodiments, the ionic liquid has a cation that is an imidazolium, and more specifically the ionic liquid has the formula:



wherein, R and R₁ are independently selected from H, an unsubstituted or substituted alkyl group having 1 to 30 carbon atoms, or an unsubstituted or substituted aryl group having 6 to 30 carbon atoms. X is an anionic group, as described hereinabove, that associates with imidazolium to form an ionic-liquid cation/anion pair.

[0015] In addition to the cation (or mixtures of cations) and anion (or mixtures of anions) of the ionic liquid, the liquid electrodeposition composition for depositing the layer comprising aluminum also comprises an aluminum salt. Aluminum salt can be introduced to the composition in the form of aluminum chloride (AlCl₃), but will tend to form different aluminum-containing ions in the ionic liquid composition, including but not limited to AlCl₄⁻ (tetrachloroaluminate) or Al₂Cl₇⁻ (heptachlorodialuminate). Aluminum-containing anions can also be introduced electrolytically by electrochemical reaction of metallic aluminum in the anode(s) of an electrochemical cell of which the electrodeposition forms a part. The electrodeposition composition can also include additives to improve the integrity of the aluminum coating such as a nucleation aid like a surfactant. Other additives are known in the art, see, e.g., US 2012/0006688 A1, and can be included as well. Organic solvents can also be present in amounts up to 30 wt. %, such as toluene, chlorobenzene, dichlorobenzenes, xylene, cyclohexane, heptane, and others.

[0016] In some embodiments, process conditions for deposition of the layer comprising aluminum can be managed to promote targeted results such as density of the aluminum layer as described in more detail below. In

practice, an electrical current is provided by a power source that is sufficient to provide an electric current density (current per effective electrode area) of at least 5 mA/cm², more specifically of at least 10 mA/cm², even more specifically at least 20 mA/cm², and even more specifically at least 30 mA/cm². Current is applied until the desired aluminum coating layer thickness is achieved (e.g., 5 μm to 50 μm). The electrodeposition method can be carried out at temperatures ranging from 20°C. to 100°C., more specifically from 20°C. to 80°C., and even more specifically from 60°C. to 70°C. The above range endpoints can be independently combined to serve as a disclosure of a number of different ranges, each of which is hereby expressly disclosed.

[0017] In some embodiments, the above-described methods can avoid conditions that can contribute to hydrogen embrittlement of the substrate 12. For example, the above-described electrolytic treatment of the substrate 12 as an anode in aqueous alkaline electrolyte can evolve oxygen at the surface of the metal substrate that can promote cleaning of the surface before electrolytic deposition of aluminum in an ionic liquid electrolyte. Cathodic electrocleaning in an acidic electrolyte, on the other hand, would evolve hydrogen at the surface of the metal substrate that could contribute to the promotion of hydrogen embrittlement of the substrate 12. Hydrogen embrittlement of the substrate 12 can be managed by post-fabrication heat treatment to drive hydrogen out of the substrate, but the effectiveness of such post-fabrication heat treatment can be limited in the case of dense aluminum overlayers, which can inhibit removal of hydrogen from the substrate. In some embodiments, the above-described methods can avoid conditions that contribute to hydrogen embrittlement, thereby allowing for deposition of higher density aluminum layers (i.e., volumetric density greater than 99%). Unlike cadmium and zinc-nickel plating on high strength steels which would require a baking process at an elevated temperature (ca. 200°C) to liberate hydrogen absorbed in the metal lattice, the methods described herein don't require baking after the coating is applied to the substrate. As mentioned above, in some embodiments, the coated article meets or exceeds requirements of the hydrogen embrittlement test as prescribed in ASTM F519-10. As used herein, the coated article meets or exceeds these requirements if the article passes the sustained load test of ASTM F519-10 of greater than 200 hours at 75% of the notch fracture strength.

[0018] In some embodiments, the layer 14 can be treated with a trivalent chromium passivation process. Such a process can be carried out by treatment of the layered substrate (e.g., by dipping or application with a brush, sponge, spray, or other coating applicator) with an aqueous solution or non-aqueous solution comprising trivalent chromium and various anions. Exemplary anions include nitrate, sulfate, phosphate, and/or acetate. Specific exemplary trivalent chromium salts can include Cr₂(SO₄)₃, (NH₄)₂Cr(SO₄)₂, KCr(SO₄)₂, CrF₃, Cr(NO₃)₃, and mix-

tures comprising any of the foregoing. Embodiments of compositions and the application thereof to substrates are described in US Patent Nos. 5,304,257, 5,374,347, 6,375,726, 6,511,532, 6,521,029, and 6,511,532. Various additives and other materials can be included in the composition comprising trivalent chromium as disclosed in the patent literature, and the trivalent chromium salt composition can be selected from any of a number of known commercially-available compositions.

[0019] While the present disclosure has been described in detail in connection with only a limited number of embodiments, it should be readily understood that the present disclosure is not limited to such disclosed embodiments. Rather, the present disclosure can be modified to incorporate any number of variations, alterations, substitutions or equivalent arrangements not heretofore described, but which are commensurate with the scope of the present invention as defined by the claims. Additionally, while various embodiments of the present disclosure have been described, it is to be understood that aspects of the present disclosure may include only some of the described embodiments. Accordingly, the present disclosure is not to be seen as limited by the foregoing description, but is only limited by the scope of the appended claims.

Claims

1. A method of coating a metal substrate, comprising disposing the metal substrate (12) as an anode in an electrolytic circuit comprising an aqueous alkaline liquid electrolyte, and applying an electrical voltage differential to the metal substrate and a cathode; and disposing the metal substrate as a cathode in an electrolytic circuit comprising a liquid electrolyte that comprises an ionic liquid and an aluminum salt, and applying an electrical voltage differential to the metal substrate and an anode to form a layer (14) comprising aluminum on the metal substrate.
2. The method of claim 1, further comprising degreasing the metal substrate prior to disposing in the aqueous alkaline liquid electrolyte.
3. The method of claims 1 or 2, further comprising grit blasting the metal substrate prior to disposing in the aqueous alkaline liquid electrolyte.
4. The method of any of claims 1-3, further comprising subjecting the metal substrate to ultrasonic cleaning prior to forming the layer comprising aluminum on the metal substrate.
5. The method of any of claims 1-4, wherein the formation of the layer comprising aluminum on the metal substrate is performed under conditions to produce the layer comprising aluminum, at a volumetric den-

sity greater than 99%.

6. The method of any of claims 1-5, wherein the metal substrate comprises steel. 5
7. The method of any of claims 1-6, wherein the electrolytic circuit comprising a liquid electrolyte that comprises an ionic liquid and an aluminum salt includes an aluminum anode. 10
8. The method of any of claims 1-7, further comprising, prior to forming the layer comprising aluminum on the metal substrate, disposing the metal substrate as an anode in an electrolytic circuit comprising a liquid electrolyte that comprises an ionic liquid, and applying an electrical voltage differential to the metal substrate and a cathode. 15
9. An article, comprising: 20
- a metal substrate (12); and
- a layer (14) comprising aluminum over the metal substrate, at a volumetric density greater than 99%, wherein said article meets or exceeds requirements hydrogen embrittlement test requirements of ASTM F519-10. 25
10. The article of claim 9, wherein the metal substrate comprises steel. 30
11. The article of claim 10, wherein the metal substrate comprises high strength low alloy steel. 35

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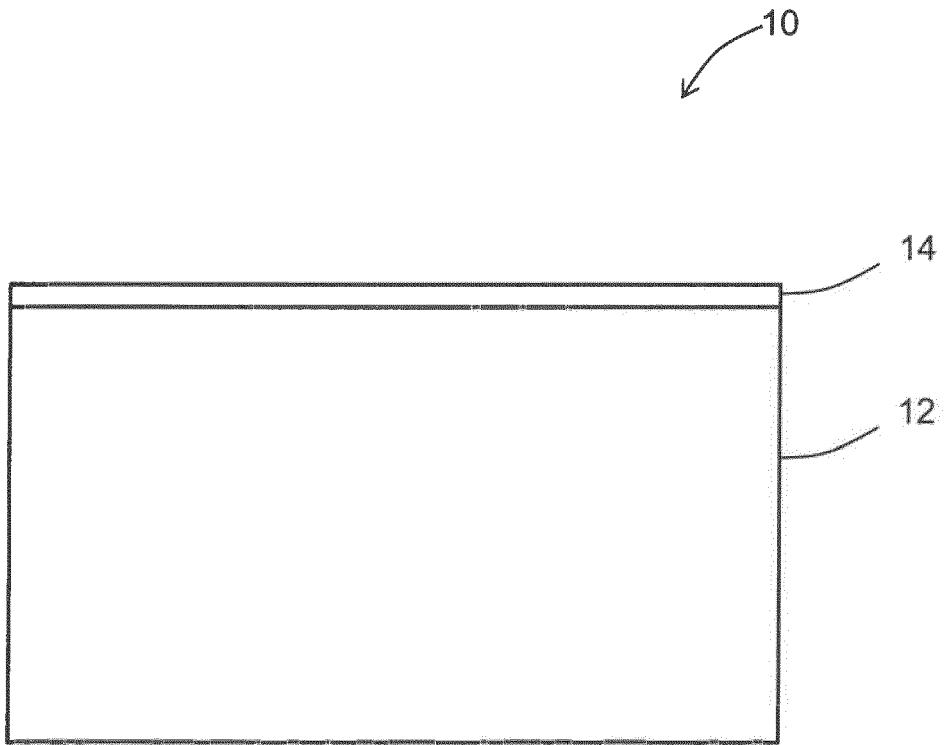


FIG. 1

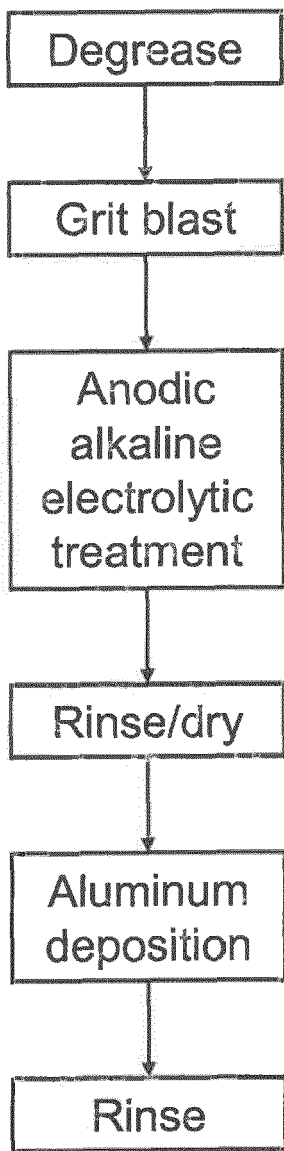


FIG. 2

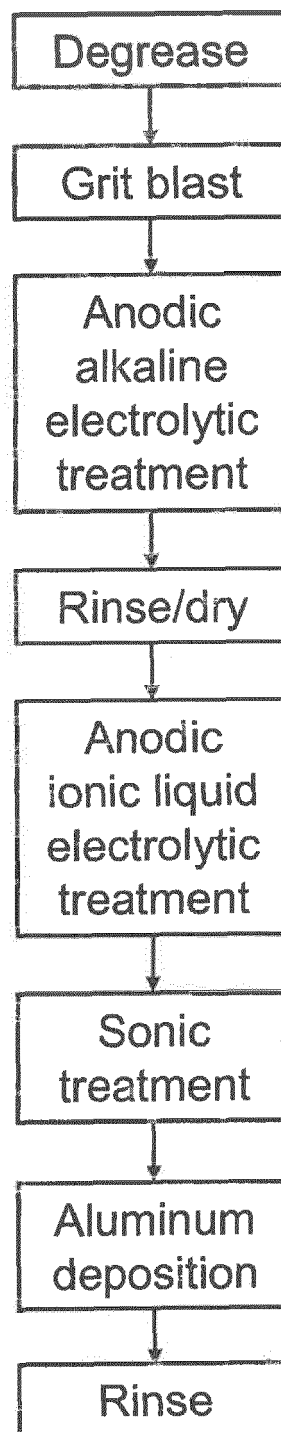


FIG. 3



EUROPEAN SEARCH REPORT

Application Number
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The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
The Hague		27 September 2018	Suárez Ramón, C
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ANNEX TO THE EUROPEAN SEARCH REPORT
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5 This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
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