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(54) Title: CORROSION RESISTANT ALUMINUM AND ALUMINUM COATING (57) Abstract Aluminum or an aluminum alloy which has not been treated with chromium and which is protected with a non-chromium aluminum conversion coating composition which has as the essential ingredients an alkaline metal permanganate and aluminum nitrate and a pH of about 2.5 to about 4.0. The composition is effective in protecting aluminum and aluminum alloys for more than 168 hours in salt fog at 95 °F according to standard ASTM method B-117. The method of coating the aluminum or aluminum alloy is generally carried out by cleaning the aluminum or aluminum alloy with sodium hydroxide, and nitric acid-hydrofluoric acid mixture, and then coating with a non-chromium aqueous conversion coating permanganate-nitrate composition. There is also provided an anodized aluminum or aluminum alloy which has not been treated with chromium, coated with a non-chromium permanganate composition.		

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S P E C I F I C A T I O N

CORROSION RESISTANT ALUMINUM AND ALUMINUM COATING

1
2 The present invention relates to corrosion resistant
3 aluminum and aluminum alloys which have not been treated with
4 chromium, a method of treating the aluminum and aluminum alloys
5 coated with a non-chromium corrosion resistant coating, and to
6 non-chromium compositions for treating the aluminum and aluminum
7 alloys.

BACKGROUND OF THE INVENTION

8
9 Aluminum and aluminum alloys have been made corrosion
10 resistant by providing a non-chromium conversion coating thereon
11 as disclosed in our U.S. Patents 4,755,224; 4,711,667; 4,895,608
12 and 4,988,396. These patents are generally related to aluminum
13 conversion coatings and although they broadly cover aluminum
14 coatings they do not specifically disclose protecting anodized
15 aluminum and/or aluminum alloys nor do these patents specifically
16 show protecting aluminum and aluminum alloys with a non-chromium
17 composition of permanganate and nitrate with a pH of less than
18 7.

19 Aluminum metal and it's alloys are in many cases anodized
20 or given an oxide film of controlled thickness in order to
21 enhance corrosion resistance, and or paint adhesion. Additional
22 corrosion resistance is necessary as the anodized oxide film is
23 quite porous and thus allows the underlining metal to be exposed
24 to corrosive agents.

25 Additional corrosion resistance is supplied by a process
26 known as sealing. One of the earliest and still most widely used

1 process, seals the surface by hydrating the oxide film in boiling
2 water or steam. (Setah, S. and Mitays, A. Proc. World Engineering
3 Congress, Tokay 1929) This causes it to swell and thus close off
4 the surface to corrosive agents. Still other early methods
5 involved converting the oxide film to aluminum silicate solution
6 U.S. Patent 1,746,153 and British Patent 393,996 (1931) with a
7 hot silicate, filling the pores with cobalt or nickel hydroxide,
8 (Speiser, C.T., Electroplating and Metal Finishings, 1956, 9, No.
9 4, 109-16, 128) and for maximum corrosion resistance U.S. Patent
10 1,946,162, hydrating the oxide film in order to seal in a
11 hexavalent chromate solution.

12 Also, the prior art prior to our above patents was mainly
13 concerned with using hexavalent chromium compositions having a
14 pH of less than 7.

15 SUMMARY OF THE INVENTION

16 Our invention eliminates some of the problems of hexavalent
17 chromium and other heavy metal compositions by providing anodized
18 aluminum and aluminum alloys with a non-chromium permanganate
19 coating; providing a non-chromium aluminum and aluminum alloy
20 conversion coating composition containing alkali metal
21 permanganate and aluminum nitrate, as the essential ingredients;
22 a method of protecting aluminum and aluminum alloys with a non-
23 chromium conversion coating containing alkali metal permanganate
24 and aluminum nitrate; and an aluminum and aluminum alloys having
25 thereon a non-chromium conversion coating of permanganate and
26 nitrate.

27 Therefore, it is an object of the present invention to
28 provide a protective coated anodized aluminum or aluminum alloy

1 which has not been treated with chromium, with a non-chromium
2 mixed metal oxide coating of manganese and aluminum oxides.

3 It is another object of the present invention to provide
4 aluminum or aluminum alloys which have not been treated with
5 chromium with a conversion coating composition that has as
6 essential ingredients alkali metal permanganate and aluminum
7 nitrate.

8 Other objects and advantages of the invention will become
9 apparent by the following description of the invention.

10 We treat the anodized aluminum and/or aluminum alloy with
11 a non-chromium alkali metal permanganate aqueous solution having
12 a pH of from about 4 to about 8. The Alkali metal is selected
13 from potassium, sodium or lithium. The preferred alkali metal
14 permanganate is sodium or potassium permanganate.

15 The alkali metal permanganate compositions may be applied
16 in any acceptable manner (i.e., immersion, spraying, misting or
17 spreading by an appropriate applicator). The anodized aluminum
18 or aluminum alloy surface is normally immersed in my aqueous
19 alkali metal permanganate solution having a concentration of
20 about 0.15 to about 0.60% by weight alkali metal permanganate
21 with a preferred concentration of about 0.3% by weight. The
22 temperature of the solution during the treatment of the oxidized
23 or anodized aluminum is between 170°F to about 212°F or the
24 boiling point of the solution.

25 The relatively high temperature is used to allow the
26 permanganate to penetrate the oxide film. Also, the temperature
27 appears to cause some swelling of the oxide film and permits the
28 production of a mixed metal oxide film of manganese and aluminum

1 oxide on the surface of the aluminum or aluminum alloy.

2 The upper concentration of the permanganate can be higher
3 than the above indicated limit of 0.6%, but anything over this
4 amount is not economically practical. The saturation limit of
5 the permanganate is the upper limit of the concentration.

6 For non-anodized aluminum or aluminum alloy, especially cast
7 aluminum and aluminum alloy, I utilize an acid composition of
8 permanganate ions and nitrate ions. The preferred permanganate
9 is the alkali metal permanganate as stated above and the nitrate
10 is aluminum nitrate.

11 The composition is effective in protecting aluminum and
12 aluminum alloys for more than 168 hours in salt fog at 95°F
13 according to standard ASTM method B-117. The process, of coating
14 the aluminum or aluminum alloy is generally carried out by
15 cleaning the aluminum or aluminum alloy with sodium hydroxide,
16 and nitric acid-hydrofluoric acid mixture, and then coating with
17 the permanganate-nitrate composition.

18 The preferred permanganate concentration is about 1.5 grams
19 per liter to about 2.3 grams per liter with the minimum
20 concentration recommended to provide 168 hours of protection
21 being 760 ppm permanganate. The preferred temperature range is
22 about 60°F to 175°F. As the temperature is raised, less
23 immersion time is necessary to form the corrosion resistant
24 coating on the aluminum or aluminum alloy surface. The most
25 preferred temperature is from about 100°F to about 175°F. The
26 preferred pH range is about 2.5 to about 4.0 with the most
27 preferred pH being about 3.5 to about 4.0. The aluminum nitrate
28 used is $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. The aluminum nitrate nine hydrate

1 concentration is about 0.10% to about 10.0% with the preferred
2 range being about 0.5% to about 2.0% $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$.

3 The permanganate-nitrate composition is particularly
4 advantageous when a relatively clear intermediate non-chromium
5 protective coating is desired. A clear coating is obtained when
6 the cast aluminum or aluminum alloy is coated for 20 seconds with
7 the permanganate-nitrate composition.

8 The cast aluminum is coated with my permanganate-nitrate
9 aqueous composition as noted above. The preferred method is by
10 immersing the cast aluminum or aluminum alloy in the aqueous
11 solution for about 20 seconds to about 2 minutes to form the non-
12 chromium conversion coating.

13 Other non-chromium compounds may be added to the
14 permanganate solutions if desired, providing the compounds do not
15 interfere with the desired corrosion resistant protection of the
16 anodized or non-anodized aluminum or aluminum alloy surfaces.

17 The cleaning compounds for the aluminum or aluminum alloy
18 surfaces are trichloroethane, sodium hydroxide, potassium
19 hydroxide, alkaline solutions of sodium nitrate, hydrofluoric
20 acid, sulfuric acid, nitric acid, sodium carbonate, sodium
21 bromate, borax, and a commercial non-ionic surfactant
22 polyoxyethylene or polyoxypropylene derivatives of organic acids,
23 alcohols, alkylphenols or amines.

24 After cleaning the aluminum or aluminum alloy surfaces, the
25 cleaned aluminum or aluminum alloy is coated with the
26 permanganate -nitrate composition or anodized and then coated
27 with the permanganate composition.

1 It is also recommended that neither the cleaning composition
2 nor the corrosion resistant alkali metal permanganate composition
3 contain a fatty acid, or any compound which would interfere with
4 adhesion or formation of a protective coating on the anodized or
5 non-anodized aluminum or aluminum alloy surface.

6 The following examples illustrate specific embodiments of
7 my invention and are not intended to limit the scope of my
8 invention to the specific embodiments shown.

9 In the following examples, all percentages are percentages
10 by weight unless otherwise indicated.

11 Examples 1-9 are directed to anodized aluminum and aluminum
12 alloys and Examples 10 to 18 are directed to protecting aluminum
13 alloys especially cast aluminum alloys with permanganate and
14 nitrate ions. The cast aluminum utilized for Examples 10 to 18
15 was an aluminum alloy casting purchased from Metal Samples,
16 Munford, Alabama 36268 and made from aluminum alloy 356.1 which
17 has more than 90% by weight aluminum and has an average
18 composition by weight of 6.5-7.5% Si, 0.25-0.40% Mg and a maximum
19 percentage of 0.5% Fe, 0.25% Cu, 0.35% Mn, 0.35% Zn, 0.25% Ti and
20 0.15% other elements as impurities.

21 The following Examples 2-4 show that when our preferred
22 limitations are not used, the panels have more pits than are
23 generally desired.

24 **EXAMPLE 1**

25 A sheet of pure aluminum metal (3"x10") was degreased with
26 trichloroethane, lightly etched in a 5% potassium hydroxide
27 solution at 70°F for two minutes, rinsed in de-ionized water,
28 deoxidized in a 3% sodium bromate - 10% nitric acid solution for

1 five minutes at 100°F and rinsed in de-ionized water for one
2 minute. The aluminum was then anodized in a solution of 5%
3 sulfuric acid and 1.0% boric acid at 80°F for 20 minutes. The
4 voltage was maintained at 15 volts and the current density at
5 about 15 amps per square foot.

6 The anodized or oxidized aluminum sheet was rinsed in cold
7 (70°F-80°F) de-ionized water for two minutes and further rinsed
8 in warm (120°F-130°F) de-ionized water for five minutes. The
9 anodized aluminum panel was then immersed in a 0.15% potassium
10 permanganate aqueous solution at 190°F-200°F for 12 minutes
11 followed by warm (120°F-130°F) water rinse for five minutes.

12 The dried permanganated treated anodized aluminum had on its
13 surface a mixed coating of aluminum and manganese oxides. This
14 permanganate treated anodized aluminum was then placed in a salt
15 fog at 95°F for 336 hours of exposure according to ASTM method
16 B-117. The panel showed no noticeable pitting.

17 EXAMPLE 2

18 A sheet of pure aluminum (3"x10") was degreased with
19 trichloroethane, lightly etched in a 5% potassium hydroxide
20 solution at 70°F for two minutes, rinsed in de-ionized water,
21 deoxidized in a 3% sodium bromate - 10% nitric acid solution for
22 five minutes at 100°F and rinsed in de-ionized water for one
23 minute. The aluminum was then anodized in a solution of 5%
24 sulfuric acid and 1.0% boric acid at 80°F for 20 minutes. The
25 voltage was maintained at 15 volts and the current density at
26 about 15 amps per square foot.

27 The anodized aluminum sheet was rinsed in cold (70°F-80°F)
28 de-ionized water for two minutes and further rinsed in warm

1 (120°F-130°F) de-ionized water for five minutes. The rinsed
2 anodized sheet of aluminum was then immersed in a 0.10% potassium
3 permanganate aqueous solution at 190°F-200° F for 12 minutes
4 followed by a warm (120°F-130°F) water rinse for five minutes.

5 The dried permanganated treated anodized aluminum had on its
6 surface a mixed coating of aluminum and manganese oxides. This
7 permanganate treated anodized aluminum was then placed in a salt
8 fog at 95°F for 336 hours of exposure according to ASTM method
9 B-117. The panel showed more than 15 pits.

10

11 **EXAMPLE 3**

12 A sheet of pure aluminum (3"x10") was degreased with
13 trichloroethane, lightly etched in a 5% potassium hydroxide
14 solution at 70°F for two minutes, rinsed in de-ionized water,
15 deoxidized in a 3% sodium bromate - 10% nitric acid solution for
16 five minutes at 100°F and rinsed in de-ionized water for one
17 minute. The aluminum was then anodized in a solution of 5%
18 sulfuric acid and 1.0% boric acid at 80°F for 20 minutes. The
19 voltage was maintained at 15 volts and the current density at
20 about 15 amps per square foot.

21 The anodized or oxidized aluminum sheet was rinsed in cold
22 (70°F-80°F) de-ionized water for two minutes and further rinsed
23 in warm (120°F-130°F) de-ionized water for five minutes. The
24 aluminum was then immersed in a 0.70% potassium permanganate
25 aqueous solution at 190°F-200°F for 12 minutes followed by a warm
26 (120°F-130°F) water rinse for five minutes.

27 The dried permanganated treated anodized aluminum had on its
28 surface a mixed coating of aluminum and manganese oxides. This

1 permanganate treated anodized aluminum was then placed in a salt
2 fog at 95°F for 336 hours of exposure according to ASTM method
3 B-117. The panel showed more than 15 pits.
4

5 EXAMPLE 4

6 A sheet of pure aluminum metal (3"x10") was degreased with
7 trichloroethane, lightly etched in a 5% potassium hydroxide
8 solution at 70°F for two minutes, rinsed in de-ionized water,
9 deoxidized in a 3% sodium bromate - 10% nitric acid solution for
10 five minutes at 100°F and rinsed in de-ionized water for one
11 minute. The aluminum was then anodized in a solution of 5%
12 sulfuric acid and 1.0% boric acid at 80°F for 20 minutes. The
13 voltage was maintained at 15 volts and the current density at
14 about 15 amps per square foot.

15 The anodized aluminum sheet was rinsed in cold (70°F-80°F)
16 de-ionized water for two minutes and further rinsed in warm
17 (120°F-130°F) de-ionized water for five minutes. The anodized
18 aluminum surface was then reacted with or "sealed" in a 0.15
19 potassium permanganate aqueous solution at 160°F for 12 minutes
20 followed by a warm (120°F-130°F) water rinse for five minutes.

21 The dried permanganated treated anodized aluminum had on its
22 surface a mixed coating of aluminum and manganese oxides. This
23 permanganate treated anodized aluminum was then placed in a salt
24 fog at 95°F for 336 hours of exposure according to ASTM method
25 B-117. The panel showed more than 15 pits.
26

EXAMPLE 5

A sheet of pure aluminum metal (3"x10") was degreased with trichloroethane, lightly etched in a 5% potassium hydroxide solution at 70°F for two minutes, rinsed in de-ionized water, deoxidized in a 3% sodium bromate - 10% nitric acid solution for five minutes at 100°F and rinsed in de-ionized water for one minute. The metal was then anodized in a solution of 5% sulfuric acid and 1.0% boric acid at 80°F for 20 minutes. The voltage was maintained at 15 volts and the current density at about 15 amps per square foot.

The anodized aluminum sheet was rinsed in cold (70°F-80°F) de-ionized water for two minutes and further rinsed in warm (120°F-130°F) de-ionized water for five minutes. The anodized aluminum surface was then immersed in a 0.15% potassium permanganate aqueous solution at 170°F for 12 minutes followed by a warm (120°F-130°F) water rinse for five minutes.

The dried permanganated treated anodized aluminum had on its surface a mixed coating of aluminum and manganese oxides. This permanganate treated anodized aluminum was then placed in a salt fog at 95°F for 336 hours of exposure according to ASTM method B-117. The panel showed no noticeable pits.

EXAMPLE 6

A sheet of pure aluminum metal (3"x10") was degreased with trichloroethane, lightly etched in a 5% potassium hydroxide solution at 70°F for two minutes, rinsed in de-ionized water, deoxidized in a 3% sodium bromate - 10% nitric acid solution for five minutes at 100°F and rinsed in de-ionized water for one

1 minute. The aluminum was then anodized in a solution of 5%
2 sulfuric acid and 1.0% boric acid at 80°F for 20 minutes. The
3 voltage was maintained at 15 volts and the current density at
4 about 15 amps per square foot.

5 The anodized aluminum sheet was rinsed in cold (70°F-80°F)
6 de-ionized water for two minutes and further rinsed in warm
7 (120°F-130°F) de-ionized water for five minutes. The anodized
8 aluminum surface was then immersed in a 0.15% potassium
9 permanganate aqueous solution at 212°F for 12 minutes followed
10 by a warm (120°F-130°F) water rinse for five minutes.

11 The dried permanganated treated anodized aluminum had on its
12 surface a mixed coating of aluminum and manganese oxides. This
13 permanganate treated anodized aluminum was then placed in a salt
14 fog at 95°F for 336 hours of exposure according to ASTM method
15 B-117. The panel showed no noticeable pits.

16 17 EXAMPLE 7

18 A sheet of "2024-T3 aluminum alloy (3"x10") was degreased
19 with trichloroethane, lightly etched in a 5% potassium hydroxide
20 solution at 70°F for two minutes, rinsed in de-ionized water,
21 deoxidized in a 3% sodium bromate - 10% nitric acid solution for
22 five minutes at 100°F and rinsed in de-ionized water for one
23 minute. The aluminum alloy was then anodized in a solution of
24 5% sulfuric acid and 1.0% boric acid at 80°F for 20 minutes. The
25 voltage was maintained at 15 volts and the current density at
26 about 15 amps per square foot.

27 The anodized aluminum alloy sheet was rinsed in cold (70°F-
28 80°F) de-ionized water for two minutes and further rinsed in warm

1 (120°F-130°F) de-ionized water for five minutes. The anodized
2 aluminum alloy surface was then immersed in a 0.3% potassium
3 permanganate aqueous solution at 190°F-200°F for 12 minutes
4 followed by a warm (120°F-130°F) water rinse for five minutes.

5 The dried permanganated treated anodized aluminum had on its
6 surface a mixed coating of aluminum and manganese oxides. This
7 permanganate treated anodized aluminum was then placed in a salt
8 fog at 95°F for 336 hours of exposure according to ASTM method
9 B-117. The panel showed no pits.

10

11 **EXAMPLE 8**

12 A sheet of "2024-T3 aluminum alloy (3"x10") was degreased
13 with trichloroethane, lightly etched in a 5% potassium hydroxide
14 solution at 70°F for two minutes, rinsed in de-ionized water,
15 deoxidized in a 3% sodium bromate - 10% nitric acid solution for
16 five minutes at 100°F and rinsed in de-ionized water for one
17 minute. The aluminum was then anodized in a solution of 5%
18 sulfuric acid and 1.0% boric acid at 80°F for 20 minutes. The
19 voltage was maintained at 15 volts and the current density at
20 about 15 amps per square foot.

21 The anodized aluminum alloy sheet was rinsed in cold (70°F-
22 80°F) de-ionized water for two minutes and further rinsed in warm
23 (120°F-130°F) de-ionized water for five minutes. The anodized
24 aluminum alloy surface was then immersed in a 0.5% potassium
25 permanganate aqueous solution at 190°F-200°F for 12 minutes
26 followed by a warm (120°F-130°F) water rinse for five minutes.

27 The dried permanganated treated anodized aluminum had on its
28 surface a mixed coating of aluminum and manganese oxides. This

1 permanganate treated anodized aluminum was then placed in a salt
2 fog at 95°F for 336 hours of exposure according to ASTM method
3 B-117. The panel showed no pits.

4
5 **EXAMPLE 9**

6 A sheet of "2024-T3 aluminum alloy (3"x10") was degreased
7 with trichloroethane, lightly etched in a 5% potassium hydroxide
8 solution at 70°F for two minutes, rinsed in de-ionized water,
9 deoxidized in a 3% sodium bromate - 10% nitric acid solution for
10 five minutes at 100°F and rinsed in de-ionized water for one
11 minute. The aluminum alloy was then anodized in a solution of
12 5% sulfuric acid and 1.0% boric acid at 80°F for 20 minutes. The
13 voltage was maintained at 15 volts and the current density at
14 about 15 amps per square foot.

15 The anodized aluminum alloy sheet was rinsed in cold (70°F-
16 80°F) de-ionized water for two minutes and further rinsed in warm
17 (120°F-130°F) de-ionized water for five minutes. The anodized
18 aluminum alloy surface was then immersed in a 0.6% potassium
19 permanganate aqueous solution at 190°F-200°F for 12 minutes
20 followed by a warm (120°F-130°F) water rinse for five minutes.

21 The dried permanganated treated anodized aluminum had on its
22 surface a mixed coating of aluminum and manganese oxides. This
23 permanganate treated anodized aluminum was then placed in a salt
24 fog at 95°F for 336 hours of exposure according to ASTM method
25 B-117. The panel showed no pits.

1 **EXAMPLE 10**

2 An aluminum alloy casting was degreased with mineral spirits
3 and cleaned and etched in 5% sodium hydroxide solution for one
4 minute at room temperature. The casting was then rinsed in
5 deionized water, acid cleaned in a 70% nitric acid, 2.4%
6 hydrofluoric acid, and 27.6% water mixture, and rinsed again in
7 deionized water. The casting, which was at room temperature, was
8 then placed in an aqueous solution having a temperature of 140°F.
9 The solution is:

10 0.10% potassium permanganate - KMnO_4
11 0.10% aluminum nitrate nine hydrate - $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$
12 99.8% water.

13 The casting remained in the solution for about 1 minute. The
14 casting was removed from the solution, rinsed and dried and
15 placed in a salt spray at 95 F for 168 hours according to ASTM
16 Standard Method B-117. The casting showed no noticeable pitting
17 in the treated area.

18

19 **EXAMPLE 11**

20 An aluminum alloy casting was degreased with mineral spirits
21 and cleaned and etched in 5% sodium hydroxide solution for one
22 minute at room temperature. The casting was then rinsed in
23 deionized water, acid cleaned in a 70% nitric acid, 2.4%
24 hydrofluoric acid, and 27.6% water mixture, and rinsed again in
25 deionized water. The room temperature casting was then placed
26 in an aqueous solution having a temperature of 140°F for about

1 1 minute. The solution is:

2 0.2% potassium permanganate

3 0.10 % $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$

4 99.7% water.

5 The casting was removed from the solution, rinsed and dried and
6 placed in a salt spray at 95°F for 168 hours according to ASTM
7 Standard Method B-117. The casting showed no noticeable pitting
8 in the treated area.

9
10 **EXAMPLE 12**

11 An aluminum alloy casting was degreased with mineral spirits
12 and cleaned and etched in 5% sodium hydroxide solution for one
13 minute at room temperature. The casting was then rinsed in
14 deionized water, acid cleaner in a 70% nitric acid, 2.4%
15 hydrofluoric acid, and 27.6% water mixture, and rinsed again in
16 deionized water. The room temperature casting was then placed in
17 an aqueous solution having a temperature of 140°F for about 1
18 minute. The solution is:

19 0.5% potassium permanganate

20 0.10% aluminum nitrate nine hydrate

21 99.4% water.

22 The casting was removed from the solution, rinsed and dried and
23 placed in a salt spray at 95°F for 168 hours according to ASTM
24 Standard Method B-117. The casting showed no noticeable pitting
25 in the treated area.

1 **EXAMPLE 13**

2 An aluminum alloy casting was degreased with mineral spirits
3 and cleaned and etched in 5% sodium hydroxide solution for one
4 minute at room temperature. The casting was then rinsed in
5 deionized water, acid cleaner in a 70% nitric acid, 2.4%
6 hydrofluoric acid, and 27.6% water mixture, and rinsed again in
7 deionized water. The room temperature casting was then placed in
8 an aqueous solution having a temperature of 140°F for about 1
9 minute. The solution is:

10 1.0% Potassium Permanganate
11 0.10% Aluminum Nitrate Nine Hydrate
12 99.9% water.

13 The casting was removed from the solution, rinsed and dried and
14 placed in a salt spray at 95°F for 168 hours according to ASTM
15 Standard Method B-117. The casting showed no noticeable pitting
16 in the treated area.

17

18 **EXAMPLE 14**

19 An aluminum alloy casting was degreased with mineral spirits
20 and cleaned and etched in 5% sodium hydroxide solution for one
21 minute at room temperature. The casting was then rinsed in
22 deionized water, acid cleaned in a 70% nitric acid, 2.4%
23 hydrofluoric acid, and 27.6% water mixture, and rinsed again in
24 deionized water. The room temperature casting was then placed in
25 an aqueous solution having a temperature of 140°F for about 1
26 minute. The solution is:

27 0.3% Potassium Permanganate
28 0.5% Aluminum Nitrate Nine Hydrate

1 99.2% water

2 The casting was removed from the solution, rinsed and dried and
3 placed in a salt spray at 95°F for 168 hours according to ASTM
4 Standard Method B-117. The casting showed no noticeable pitting
5 in the treated area.

6 **EXAMPLE 15**

7 An aluminum alloy casting was degreased with mineral spirits
8 and cleaned and etched in 5% sodium hydroxide solution for one
9 minute at room temperature. The casting was then rinsed in
10 deionized water, acid cleaner in a 70% nitric acid, 2.4%
11 hydrofluoric acid, and 27.6% water mixture, and rinsed again in
12 deionized water. The room temperature casting was then placed in
13 an aqueous solution having a temperature of 140°F for about 1
14 minute. The solution is:

15 0.3% Potassium Permanganate

16 1.0% Aluminum Nitrate Nine Hydrate

17 98.7% water.

18 The casting was removed from the solution, rinsed and dried and
19 placed in a salt spray at 95°F for 168 hours according to ASTM
20 Standard Method B-117. The casting showed no noticeable pitting
21 in the treated area.

22

23 **EXAMPLE 16**

24 An aluminum alloy casting was degreased with mineral spirits
25 and cleaned and etched in 5% sodium hydroxide solution for one
26 minute at room temperature. The casting was then rinsed in
27 deionized water, acid cleaned in a 70% nitric acid, 2.4%
28 hydrofluoric acid, and 27.6% water mixture, and rinsed again in

1 deionized water. The room temperature casting was then placed in
2 an aqueous solution having a temperature of 140°F for about 1
3 minute. The solution is:

4 0.3% Lithium Permanganate

5 2.0% Aluminum Nitrate Nine Hydrate

6 98.7% water.

7 The casting was removed from the solution, rinsed and dried and
8 placed in a salt spray at 95°F for 168 hours according to ASTM
9 Standard Method B-117. The casting showed no noticeable pitting
10 in the treated area .

11 EXAMPLE 17

12 An aluminum alloy casting was degreased with mineral spirits
13 and cleaned and etched in 5% sodium hydroxide solution for one
14 minute at room temperature. The casting was then rinsed in
15 deionized water, acid cleaned in a 70% nitric acid, 2.4%
16 hydrofluoric acid, and 27.6% water mixture and rinsed again in
17 deionized water. The room temperature casting was then placed in
18 an aqueous solution having a temperature of 140°F for about 1
19 minute. The solution is:

20 0.3% Potassium Permanganate

21 1.0% Aluminum Nitrate Nine Hydrate

22 98.7% water

23 The casting was removed from the solution, rinsed and dried and
24 placed in a salt spray at 95°F for 168 hours according to ASTM
25 Standard Method B-117. The casting showed no noticeable pitting
26 in the treated area.
27
28

EXAMPLE 18

An aluminum alloy casting was degreased with mineral spirits and cleaned and etched in 5% sodium hydroxide solution for one minute at room temperature. The casting was then rinsed in deionized water, acid cleaned in a 70% nitric acid, 2.4% hydrofluoric acid, and 27.6% water mixture, and rinsed again in deionized water. The room temperature casting was then placed in an aqueous solution having a temperature of 140°F for about 1 minute. The solution is:

03% Potassium Permanganate

1.0% Aluminum Nitrate Nine Hydrate

98.7% water

The casting was removed from the solution, rinsed and dried and placed in a salt spray at 95°F for 168 hours according to ASTM Standard Method B-117. The casting showed no noticeable pitting in the treated area.

1 I CLAIM:

- 2 1. Aluminum or aluminum alloy which has not been treated with
3 chromium, coated with a non-chromium aqueous composition
4 containing as the essential ingredients thereof an alkali
5 metal permanganate and an aluminum nitrate.
- 6 2. The aluminum or aluminum alloy of claim 1 wherein the
7 permanganate is potassium permanganate.
- 8 3. The aluminum or aluminum alloy of claim 1 wherein the
9 composition is an aqueous composition having a pH of about
10 2.5 to about 4.0, there is at least 760 ppm of permanganate
11 and there is about 0.10 to about 10.0% of aluminum nitrate.
- 12 4. The aluminum or aluminum alloy of claim 3 wherein there is
13 at least 1.5 gms of alkali metal permanganate per liter,
14 the nitrate is $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and the nitrate concentration
15 is about 0.5% to about 2.0%.
- 16 5. A corrosion resistant anodized aluminum or aluminum alloy
17 which has not been treated with chromium, coated with a
18 non-chromium mixed metal oxide coating of manganese and
19 aluminum oxides.
- 20 6. The corrosion resistant anodized aluminum or aluminum alloy
21 of claim 5 which is coated with a non-chromium composition
22 of alkali metal permanganate to provide the mixed metal
23 oxide coating and wherein the alkali metal is selected from
24 the group consisting of sodium, potassium, and lithium.

25

- 1 7. A method of protecting aluminum or aluminum alloy with a
2 non-chromium coating comprising contacting the aluminum or
3 aluminum alloy with an aqueous solution containing as the
4 essential ingredients thereof an alkali metal permanganate
5 and an aluminum nitrate, the aqueous coating solution
6 contains at least 760 ppm of permanganate, and about 0.10
7 to 10.0% of aluminum nitrate, maintaining the pH of the
8 solution at about 2.5 to about 4.0, maintaining the
9 temperature of the solution at about 140° to 170°F,
10 immersing the aluminum or aluminum alloy in the solution
11 for at least 20 seconds to form a protective conversion
12 coating on the aluminum or aluminum alloy and removing any
13 excess coating solution from the aluminum or aluminum
14 alloy.
- 15 8. The method of claim 7 wherein the aqueous coating solution
16 contains at least about 1.5 gms of sodium permanganate per
17 liter of solution and about 0.5% to about 2.0% by weight of
18 $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$.
- 19 9. A non-chromium aluminum coating composition to provide a
20 protective conversion coating for aluminum or aluminum
21 alloys comprising as the essential ingredients thereof an
22 alkali metal permanganate and an aluminum nitrate.
- 23 10. The composition of claim 9 wherein the permanganate is
24 potassium permanganate.
- 25 11. The composition of claim 9 wherein the composition is an
26 aqueous composition having a pH of about 2.5 to about 4.0,
27 there is at least 760 ppm of permanganate and there is
28 about 0.10 to about 10.0% of aluminum nitrate.

1 12. The composition of claim 11 wherein there is at least 1.5
2 gms of alkali metal permanganate per liter, the nitrate is
3 $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and the nitrate concentration is about 0.5% to
4 about 2.0%.

5

INTERNATIONAL SEARCH REPORT

 International application No.
PCT/US95/14057

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C23C 22/56; C23F 11/18; B32B 9/00

US CL : 148/272; 205/201,203,204; 106/14.21; 428/472.1, 472.2

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 148/272; 205/201,203,204; 106/14.21; 428/472.1, 472.2

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,755,224 (BIBBER) 05 July 1988, col.2, lines 40-60.	1-6
Y	US, A, 1,971,240 (TOSTERUD ET AL) 21 August 1934, page 1, lines 70-90	1--6
Y	US, A, 4,878,963 (BIBBER) 07 November 1989, col. 2, lines 60-65.	1-6

☐ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	*T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A document defining the general state of the art which is not considered to be of particular relevance	*X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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*O document referring to an oral disclosure, use, exhibition or other means	
*P document published prior to the international filing date but later than the priority date claimed	

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