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(54) METAL SURFACE TREATMENT SOLUTION AND METAL SURFACE TREATMENT METHOD

(57) Provided is a metal surface treatment solution and a metal surface treatment method, which can color a metal surface into a grayish color tone with good treatment efficiency. The metal surface treatment solution contains tellurium, a tellurium compound, or a salt thereof.

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Description

TECHNICAL FIELD

[0001] The present invention relates to a metal surface treatment solution and a metal surface treatment method.

BACKGROUND ART

[0002] Conventionally, in coloring of various metals, in particular aluminum or an aluminum alloy, it is known to adsorb a dye onto an anodized coating or an anodic oxidation coating in order to obtain a grayish color tone.

[0003] For example, Patent Document 1 discloses a method for electrolytically coloring aluminum and an aluminum alloy, comprising providing a coating structure capable of electrolytic coloring, from a colored coating formed on a base surface of aluminum or the aluminum alloy due to electrolytic coloring or spontaneous coloring; and then carrying out electrolytic coloring to superimpose the colors to obtain a coating having a new color tone. It also discloses that according to such a structure, it is possible to provide an electrolytic coloring method that can obtain various color tones including various intermediate colors, which would not otherwise be obtained by the conventional electrolytic coloring method.

CITATION LIST

Patent Literatures

[0004] Patent Document 1: Japanese Patent Application Publication No. S60-110895 A

SUMMARY OF INVENTION

Technical Problem

[0005] However, conventionally, in order to color the metal surface into a grayish color tone, it is necessary to use alumite, for example, if the metal to be colored is aluminum or an aluminum alloy. That is, in order to color the metal surface into a grayish color tone it is necessary to use a metal having an oxide film on the surface, so that there are many treatment steps. Therefore, there is a need for improvement of treatment efficiency.

[0006] In view of such problems, an object of the present invention is to provide a metal surface treatment solution and a metal surface treatment method, which can color a metal surface into a grayish color tone with good treatment efficiency.

Solution to Problem

[0007] As a result of intensive researches to solve the above problems, the present inventors have found that a treatment with a metal surface treatment solution containing tellurium or a tellurium compound or a salt thereof can allow the metal surface to be colored into a grayish color tone with good treatment efficiency.

[0008] In one aspect, the present invention completed on the basis of the above findings is a metal surface treatment solution, comprising tellurium, a tellurium compound, or a salt thereof.

[0009] In one embodiment of the metal surface treatment solution according to the present invention, the tellurium or the tellurium compound or the salt thereof is tellurium monoxide, tellurium dioxide, tellurium trioxide, tellurous acid, telluric acid, tellurium tetrachloride, dimethyl telluride, or a salt thereof, or a combination thereof.

[0010] In another embodiment of the metal surface treatment solution according to the present invention, a total content of the tellurium, the tellurium compound or the salt thereof is from 0.5 to 100 g/L.

[0011] In still another embodiment, the metal surface treatment solution according to the present invention further comprises an inorganic acid or a salt thereof.

[0012] In still another embodiment of the metal surface treatment solution according to the present invention, the inorganic acid or the salt thereof is sulfuric acid, nitric acid, hydrochloric acid, phosphoric acid, or a salt thereof, or a combination thereof.

[0013] In still another embodiment of the metal surface treatment solution according to the present invention, a total content of the inorganic acid or the salt thereof is from 1 to 200 g/L.

[0014] In still another embodiment, the metal surface treatment solution according to the present invention further comprises an organic sulfur compound or a salt thereof.

[0015] In still another embodiment of the metal surface treatment solution according to the present invention, the organic sulfur compound or the salt thereof is thiourea, thiourea dioxide, thiodiglycol, dimethylthiourea, thiomalic acid, dithiodiglycolic acid, dimethylsulfoxide, methanesulfonic acid, p-toluenesulfonic acid, p-phenolsulfonic acid, thiocyanic acid, cysteine, methionine, or a salt thereof, or a combination thereof.

[0016] In still another embodiment of the metal surface treatment solution according to the present invention, a total content of the organic sulfur compound or the salt thereof is from 0.1 to 50 g/L.

[0017] In still another embodiment, the metal surface treatment solution according to the present invention further comprises a carboxylic acid or a hydroxycarboxylic acid, or a salt thereof.

[0018] In still another embodiment of the metal surface treatment solution according to the present invention, the carboxylic acid or the hydroxycarboxylic acid or the salt thereof is formic acid, acetic acid, propionic acid, lactic acid, malic acid, citric acid, oxalic acid, gluconic acid, malonic acid, succinic acid, benzoic acid, pyruvic acid, glyoxylic acid, nitrilotriacetic acid, ethylenediaminetetraacetic acid, or a salt thereof, or a combination thereof.

[0019] In still another embodiment of the metal surface treatment solution according to the present invention, a total content of the carboxylic acid or the hydroxycarboxylic acid or the salt thereof is from 0.5 to 100 g/L.

[0020] In still another embodiment, the metal surface treatment solution according to the present invention further comprises an oxo acid or a salt thereof.

[0021] In still another embodiment of the metal surface treatment solution according to the present invention, the oxo acid or the salt thereof is perchloric acid, chloric acid, chlorous acid, hypochlorous acid, bromic acid, carbonic acid, boric acid, or a salt thereof, or a combination thereof.

[0022] In still another embodiment of the metal surface treatment solution according to the present invention, a total content of the oxo acid or the salt thereof is from 0.5 to 100 g/L.

[0023] In still another embodiment of the metal surface treatment solution according to the present invention, the metal to be treated is at least one selected from the group consisting of aluminum, aluminum alloys, copper, copper alloys, iron, iron alloys, zinc, zinc alloys, nickel, nickel alloys, magnesium, and magnesium alloys.

[0024] In another aspect, the present invention is a metal surface treatment method comprising a step of coloring a metal using the metal surface treatment solution according to the present invention.

[0025] In one embodiment of the metal surface treatment method according to the present invention, in the step of coloring the metal, the metal is immersed in the metal surface treatment solution at a temperature of from 10 °C to 80 °C for 10 seconds to 20 minutes to color the metal.

Advantageous Effects of Invention

[0026] According to the present invention, it is possible to provide a metal surface treatment solution and a metal surface treatment method, which can color a metal surface into a grayish color tone with good treatment efficiency.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0027] Hereinafter, embodiments of a metal surface treatment solution and a metal surface treatment method according to the present invention will be described. However, the present invention is not limited to the embodiments, and various changes, modifications, and improvements may be added without departing from the scope of the present invention, based on knowledge of those skilled in the art.

(Metal Surface Treatment Solution)

[0028] A metal surface treatment solution according to an embodiment of the present invention contains tellurium, a tellurium compound, or a salt thereof. By using the metal surface treatment solution containing tellurium, the tellurium compound, or the salt thereof, a coating (colored coating) can be formed on the metal surface simply by immersing a metal to be treated in the metal surface treatment solution, whereby the metal surface can be colored into a grayish color tone. Therefore, when the metal surface is colored into a grayish color tone, there is no need to form an oxide film on the surface of the metal, and there is no need to color the metal by electrolysis, resulting in an improved treatment efficiency. Further, according to the metal surface treatment solution according to an embodiment of the present invention, adhesion of the coating (colored coating) formed on the metal surface is also improved.

(Metal To Be Treated)

[0029] A metal whose surface is to be colored with the metal surface treatment solution according to an embodiment of the present invention (a metal to be treated) includes at least one selected from the group consisting of aluminum, aluminum alloys, copper, copper alloys, iron, iron alloys, zinc, zinc alloys, nickel, nickel alloys, magnesium, and magnesium alloys. The metal to be treated may be the metal itself, for example, a plating of the metal formed on a surface of a metal substrate such as an iron-based material or an iron-based component.

(Tellurium or Tellurium Compound or Salt Thereof)

[0030] Tellurium or the tellurium compound or the salt thereof is preferably tellurium monoxide, tellurium dioxide, tellurium trioxide, tellurous acid, telluric acid, tellurium tetrachloride, dimethyl telluride, or a salt thereof, or a combination thereof. The salts of tellurium monoxide, tellurium dioxide, tellurium trioxide, tellurous acid, telluric acid, tellurium tetrachloride, and dimethyl telluride that can be used include metal salts or ammonium salts of them.

[0031] The total content of tellurium or the tellurium compound or the salt thereof in the metal surface treatment solution according to an embodiment of the present invention depends on a type of a metal to be treated, and on a degree of grayish color tone to be developed, and, for example, the total content of tellurium or the tellurium compound or the salt thereof can be from 0.5 to 100 g/L. Basically, as the total content of tellurium, the tellurium compound or the salt thereof is lower, the surface of the metal can be colored into a lighter grayish color tone. Further, as the total content of tellurium, the tellurium compound or the salt thereof is higher, the surface of the metal can be colored into a darker grayish color tone. The total content of tellurium, the tellurium compound or the salt thereof is more preferably from 1 to 50 g/L, and even more preferably from 2 to 20 g/L.

[0032] The metal surface treatment solution according to an embodiment of the present invention may contain an inorganic acid or a salt thereof, an organic sulfur compound or a salt thereof, a carboxylic acid or a hydroxycarboxylic acid or a salt thereof, an oxo acid or a salt thereof, as described below. However, for the metal surface treatment solution that does not contain these components, the surface of the metal such as aluminum and aluminum alloys can be colored into a grayish tone having more improved appearance.

(Inorganic Acid or Salt Thereof)

[0033] The metal surface treatment solution according to an embodiment of the present invention may further contain an inorganic acid or a salt thereof. Even if the metal surface treatment solution according to an embodiment of the present invention contains the inorganic acid or the salt thereof, the surface of the metal to be treated can be colored into a grayish color tone with good treatment efficiency. Further, the metal surface treatment solution according to an embodiment of the present invention contains the inorganic acid or the salt thereof, whereby dissolution of the metal is promoted and a pH of the metal surface is increased, so that reaction for forming a colored coating is promoted. Therefore, the metal surface treatment solution according to an embodiment of the present invention can color the surface of the metal such as, in particular, copper, copper alloys, iron, iron alloys, zinc, zinc alloys, nickel, nickel alloys, magnesium, and magnesium alloys into a grayish color tone that has more improved appearance.

[0034] The inorganic acid or the salt thereof is preferably sulfuric acid, nitric acid, hydrochloric acid, phosphoric acid, or a salt thereof, or a combination thereof. The salts of sulfuric acid, nitric acid, hydrochloric acid and phosphoric acid that can be used include metal salts or ammonium salts of those acids.

[0035] The total content of the inorganic acid or the salt thereof in the metal surface treatment solution according to an embodiment of the present invention can be from 1 to 200 g/L. Basically, as the total content of the inorganic acid or the salt thereof is lower, the surface of the metal can be colored into a lighter grayish color tone. Further, as the total content of the inorganic acid or the salt thereof is higher, the metal surface can be colored into a deeper grayish color tone. The total content of the inorganic acid or the salt thereof is more preferably from 10 to 150 g/L, and even more preferably from 70 to 120 g/L.

(Organic Sulfur Compound or Salt Thereof)

[0036] The metal surface treatment solution according to an embodiment of the present invention may further contain an organic sulfur compound or a salt thereof. Even if the metal surface treatment solution according to an embodiment of the present invention contains the organic sulfur compound or the salt thereof, the surface of the metal to be treated can be colored into a grayish color tone with good treatment efficiency. Further, the metal surface treatment solution according to an embodiment of the present invention contains the organic sulfur compound or the salt thereof, whereby dissolution of the metal is promoted and a pH of the metal surface is increased, so that reaction for forming a colored coating is promoted. Therefore, the metal surface treatment solution according to an embodiment of the present invention can color the surface of the metal such as, in particular, copper, copper alloys, nickel and nickel alloys into a grayish color tone that has more improved appearance.

[0037] When the organic sulfur compound or the salt thereof may preferably be thiourea, thiourea dioxide, thiodiglycol, dimethylthiourea, thiomalic acid, dithiodiglycolic acid, dimethyl sulfoxide, methanesulfonic acid, p-toluenesulfonic acid, p-phenolsulfonic acid, thiocyanic acid, cysteine, methionine, or salts thereof, or combinations thereof. The salts of thiourea, thiourea dioxide, thiodiglycol, dimethylthiourea, thiomalic acid, dithiodiglycolic acid, dimethylsulfoxide, methanesulfonic acid, p-toluenesulfonic acid, p-phenolsulfonic acid, thiocyanic acid, cysteine, and methionine that can be used include metal salts or ammonium salts of those acids.

[0038] The total content of the organic sulfur compound or the salt thereof in the metal surface treatment solution according to an embodiment of the present invention can be from 0.1 to 50 g/L. Basically, as the total content of the organic sulfur compound or the salt thereof is lower, the surface of the metal can be colored into a lighter grayish color tone. Further, as the total content of the organic sulfur compound or the salt thereof is higher, the surface of the metal can be colored into a darker grayish color tone. The total content of the organic sulfur compound or the salt thereof is more preferably from 1 to 30 g/L, and even more preferably from 5 to 15 g/L.

(Carboxylic Acid or Hydroxycarboxylic Acid, or Salt Thereof)

[0039] The metal surface treatment solution according to an embodiment of the present invention may further contain a carboxylic acid or a hydroxycarboxylic acid, or a salt thereof. Even if the metal surface treatment solution according to an embodiment of the present invention contains the carboxylic acid or the hydroxycarboxylic acid, or the salt thereof, the surface of the metal to be treated can be colored into a grayish color tone with good treatment efficiency. Further, the metal surface treatment solution according to an embodiment of the present invention contains the carboxylic acid or the hydroxycarboxylic acid, or the salt thereof, whereby the carboxylic acid or the hydroxycarboxylic acid is chelated with tellurium, thereby suppressing a coloring reaction and tending to form a dense coating. Therefore, the surface of the metal such as, in particular copper, copper alloys, iron, iron alloys, zinc and zinc alloys can be colored in a grayish color tone that has more improved appearance.

[0040] The carboxylic acid or the hydroxycarboxylic acid, or the salt thereof may preferably be formic acid, acetic acid, propionic acid, lactic acid, malic acid, citric acid, oxalic acid, gluconic acid, malonic acid, succinic acid, benzoic acid, pyruvic acid, glyoxylic acid, nitrilotriacetic acid, ethylenediaminetetraacetic acid, or salts thereof, or combinations thereof. The salts of formic acid, acetic acid, propionic acid, lactic acid, malic acid, citric acid, oxalic acid, gluconic acid, malonic acid, succinic acid, benzoic acid, pyruvic acid, glyoxylic acid, nitrilotriacetic acid, and ethylenediaminetetraacetic acid that can be used include metal salts or ammonium salts of those acids.

[0041] The total content of the carboxylic acid or the hydroxycarboxylic acid or the salt thereof in the metal surface treatment solution according to an embodiment of the present invention can be from 0.5 to 100 g/L. Basically, as the total content of the carboxylic acid or the hydroxycarboxylic acid or the salt thereof is lower, the surface of the metal can be colored into a darker grayish color tone. Further, as the total content of the carboxylic acid or the hydroxycarboxylic acid or the salt thereof is higher, the surface of the metal can be colored into a lighter grayish color tone. The total content of the carboxylic acid or the hydroxycarboxylic acid or the salt thereof is more preferably from 1 to 50 g/L, and even more preferably from 10 to 30 g/L.

(Oxo Acid or Salt Thereof)

[0042] The metal surface treatment solution according to an embodiment of the present invention may further contain an oxo acid or a salt thereof. Even if the metal surface treatment solution contains the oxo acid or the salt thereof, the surface of the metal to be treated can be colored into a grayish color with good treatment efficiency. Further, the metal surface treatment solution according to an embodiment of the present invention contains the oxo acid or the salt thereof, whereby the surface of the metal such as, in particular copper, copper alloys, iron, iron alloys, zinc and zinc alloys can be colored in a grayish color tone that has more improved appearance.

[0043] The oxo acid or the salt thereof may preferably be perchloric acid, chloric acid, chlorous acid, hypochlorous acid, bromic acid, carbonic acid, boric acid, or salts thereof, or combinations thereof. The salts of perchloric acid, chloric acid, chlorous acid, hypochlorous acid, bromic acid, carbonic acid, and boric acid that can be used include metal salts or ammonium salts of those acids.

[0044] The total content of the oxo acid or the salt thereof in the metal surface treatment solution according to an embodiment of the present invention can be from 0.5 to 100 g/L. Basically, as the total content of the oxo acid or the salt thereof is lower, the surface of the metal can be colored into a lighter grayish color tone. Further, as the total content of the oxo acid or the salt thereof is higher, the surface of the metal can be colored into a darker grayish color tone. The total content of the oxo acid or the salt thereof is more preferably from 1 to 50 g/L, and even more preferably from 10 to 30 g/L.

(Aqueous Medium)

[0045] The metal surface treatment solution according to an embodiment of the present invention may be a mixture of the various components as described above and an aqueous medium. The aqueous medium refers to a medium containing water as a main component. Examples of the aqueous medium include a medium containing water as a main component and an organic solvent such as an alcohol miscible with water. During the preparation of the metal surface treatment solution according to an embodiment of the present invention, during storage of the metal surface treatment solution, or after coloring of the surface of the metal, the aqueous medium may optionally contain various components that advantageously act to improve any property of the colored surface of the metal, or various components that do not substantially inhibit the effects of the present invention. Specific examples of these components include pH adjusting agents, storage stabilizers and the like.

(Metal Surface Treatment Method)

[0046] Next, a metal surface treatment method according to an embodiment of the present invention will be described in detail. First, a bath is prepared that contains the metal surface treatment solution according to the embodiment of the present invention. The metal to be treated is then immersed in the metal surface treatment solution while controlling a temperature of the metal surface treatment solution in the bath. After a certain period of time, the metal to be treated is pulled up from the bath to obtain a metal having a surface colored into a grayish color tone. Thus, according to the metal surface treatment method according to the embodiment of the present invention, only immersion of the metal to be treated in the metal surface treatment solution can allow the surface of the metal to be colored into the grayish color tone. Therefore, when coloring the surface of the metal, it is not necessary to form an oxide film on the surface of the metal, and it is not necessary to perform coloring by electrolysis, thereby improving the treatment efficiency.

[0047] Further, in the metal surface treatment method according to the embodiment of the present invention, the surface of the metal to be treated may be colored, for example by bringing the surface treatment solution into contact with the surface of the metal, for example in a spraying step of the metal surface treatment solution, in addition to the immersion of the metal to be treated in the metal surface treatment solution.

[0048] A treatment temperature with the metal surface treatment solution is preferably in a range of from 10 to 80 °C, and more preferably in a range of from 10 to 60 °C, and even more preferably in a range of from 30 to 60 °C. When the treatment temperature is 10 °C or more, a reaction velocity of the surface treatment increases, and when the treatment temperature is 80 °C or less, a decrease in a liquid level of the metal surface treatment solution due to evaporation can be suppressed.

[0049] A treatment time with the metal surface treatment solution is preferably in a range of from 10 seconds to 20 minutes, and more preferably in a range of from 30 seconds to 20 minutes, and even more preferably in a range of from 1 minute to 10 minutes. Basically, as the treatment time is shorter, the surface of the metal can be colored into a lighter grayish color tone. Further, as the treatment time is longer, the surface of the metal can be colored into a darker grayish color tone.

[0050] When carrying out the metal surface treatment, the metal to be treated can be previously degreased, activated, or surface-adjusted to improve the appearance, corrosion resistance and reactivity with the metal surface treatment solution of the metal to be treated.

[0051] After the metal surface treatment, a post-treatment may be carried out with coating agents containing one or more selected from the group consisting of silicon, a resin and a wax. These coating agents are not particularly limited as long as they do not affect the desired color tone on the surface of the metal, and include coating agents containing resins such as acrylic resins, olefin resins, alkyd resins, urea resins, epoxy resins, melamine resins, fluororesins, polyethylene, polyvinyl chloride, polystyrene, polypropylene, methacrylic resins, phenolic resins, polyester resins, polyurethane, polyamide, and polycarbonate, and silicates, colloidal silica or the like. The concentration of those resins is preferably from 0.01 to 800 g/L, although the appropriate concentration varies depending on the type of resins. Specific examples of the coating agents include Cosmer Coat (trade name; from Kansai Paint Co., Ltd.); High Seal 272 (trade name; from NIPPON HYOMEN KAGAKU KABUSHIKI KAISHA); Stron JS Coat (trade name; NIPPON HYOMEN KAGAKU KABUSHIKI KAISHA); Triner TR-170 (trade name; NIPPON HYOMEN KAGAKU KABUSHIKI KAISHA); Finigard (trade name; from Coventya) and the like. Specific examples of acrylic resins include Hirotite (trade name ; Hitachi Chemical Co., Ltd.) and Alloset (trade name; Nippon Shokubai Co., Ltd.). Specific examples of the olefin resins include FLO-THENE (trade name; SUMITOMO SEIKA CHEMICALS CO., LTD.); PES (trade name; Nippon Unicar Co., Ltd.); CHEMIPEARL (trade name; Mitsui Chemicals, Inc.); and SUNFINE (trade name; Asahi Kasei Corporation) and the like.

[0052] The metal surface treatment solution according to the embodiment of the present invention can be used for the purpose of coloring the metal surface into a desired color, imparting a desired aesthetic appearance, or imparting distinctiveness, or the like. As a form of the metal to be treated, any form can be used, and there is no particular limitation. For example, decorative articles, fastening members such as buttons and fasteners, parts for vehicles, and the like can be used. The shape of the metal to be treated is not limited, and any shape can be used.

EXAMPLES

[0053] Hereinafter, while Examples of the present invention will be described, these Examples are provided for better understanding of the present invention, and are not intended to limit the present invention.

[Test Example 1: Coloring Test for Aluminum and Aluminum Alloy]

(Examples 1 to 35, 92, 93)

[0054] JIS A5052 (aluminum-magnesium alloy) and ADC12 (aluminum die-cast) were prepared as specimens (metal pieces to be treated), and the surfaces of the specimens were sequentially degreased and washed with water.

[0055] A bath containing each metal surface treatment solution having each solution composition as shown in Tables 1 to 3 and 8 were prepared. Pure water was used as an aqueous medium of the metal surface treatment solution.

[0056] Subsequently, each specimen was immersed while controlling the metal surface treatment solution in the bath at each temperature as shown in Tables 1 to 3 and 8. After immersion for each time as shown in Tables 1 to 3 and 8, each specimen was taken out. The surface of each specimen was washed with water and then dried.

[0057] In Examples 92 and 93, each specimen after forming a coating (a colored coating) by immersion were washed with water, subjected to a coating treatment, and dried. For the coating treatment in Example 92, Stron JS Coat (a coating agent from NIPPON HYOMEN KAGAKU KABUSHIKI KAISHA) was used, and for the coating treatment in Example 93, TR-170 (a coating agent from NIPPON HYOMEN KAGAKU KABUSHIKI KAISHA) was used.

[Test Example 2: Coloring Test for Copper and Copper Alloy]

(Examples 36 to 55)

[0058] JIS C2600P (brass) and C1100P (pure copper) were prepared as specimens (metal pieces to be treated), and the surfaces of the specimens were sequentially degreased and washed with water.

[0059] A bath containing each surface treatment solution having each solution composition as shown in Tables 4 and 5 was prepared. Pure water was used as an aqueous medium of the metal surface treatment solution.

[0060] Subsequently, each specimen was immersed while controlling the metal surface treatment solution in the bath at each temperature as shown in Tables 4 and 5. After immersion for each time as shown in Tables 4 and 5, each specimen was taken out. Subsequently, the surface of each specimen was washed with water and then dried.

[Test Example 3: Coloring Test for Zinc and Zinc Alloy]

(Examples 56 to 75)

[0061] JIS ZDC2 (zinc die-cast) and a zinc plating material were prepared as specimens (metal pieces to be treated), and the surfaces of the specimens were sequentially degreased and washed with water. The zinc plating material was obtained by forming a zincate zinc plating having a thickness of 8 μm onto a base material of JIS SPCC (rolled steel sheet) as defined in the JIS standard. Further, 9000 ABS from NIPPON HYOMEN KAGAKU KABUSHIKI KAISHA was used as a brightener for the zincate zinc plating.

[0062] A bath was then prepared that contained each metal surface treatment solution having each solution composition as shown in Tables 6 and 7. Pure water was used as an aqueous medium of the metal surface treatment solution.

[0063] Subsequently, each specimen was immersed while controlling the metal surface treatment solution in the bath at each temperature as shown in Tables 6 and 7. After immersion for each time as shown in Tables 6 and 7, each specimen was taken out. Subsequently, the surface of each specimen was washed with water and then dried.

[Test Example 4: Coloring Test for Iron and Iron Alloy]

(Examples 76 to 80)

[0064] JIS SPCC (rolled steel sheet) was prepared as a specimen (a metal piece to be treated), and the surface of the specimen was sequentially degreased and washed with water. A bath was then prepared that contained each metal surface treatment solution having each solution composition as shown in Table 7. Pure water was used as an aqueous medium of the metal surface treatment solution.

[0065] Subsequently, each specimen was immersed while controlling the metal surface treatment solution in the bath at each temperature as shown in Table 7. After immersion for each time as shown in Table 7, each specimen was taken out. Subsequently, the surface of each specimen was washed with water and then dried.

[Test Example 5: Coloring Test for Magnesium and Magnesium Alloy]

(Examples 81 to 86)

[0066] JIS AZ31 and JIS AZ91 (magnesium-zinc alloy) were prepared as specimens (metal pieces to be treated), and the surfaces of the specimens were sequentially degreased and washed with water.

[0067] Subsequently, a bath was then prepared that contained each metal surface treatment solution having each solution composition as shown in Table 8. Pure water was used as an aqueous medium of the metal surface treatment solution.

[0068] Subsequently, each specimen was immersed while controlling the metal surface treatment solution in the bath at each temperature as shown in Table 8. After immersion for each time shown in Table 8, each specimen was taken out. Subsequently, the surface of each specimen was washed with water and then dried.

[Test Example 6: Coloring Test for Nickel and Nickel Alloy]

(Examples 87 to 91)

[0069] JIS Ni200 (pure nickel) was prepared as a specimen (a metal piece to be treated), and the surface of the specimen was sequentially degreased and washed with water.

[0070] A bath was then prepared that contained each metal surface treatment solution having each solution composition as shown in Table 8. Pure water was used as an aqueous medium of the metal surface treatment solution.

[0071] Subsequently, each specimen was immersed while controlling the metal surface treatment solution in the bath at each temperature as shown in Table 8. After immersion for each time as shown in Table 8, each specimen was taken out. Subsequently, the surface of each specimen was washed with water and then dried.

[Test Example 7]

(Comparative Examples 1 to 10)

[0072] Metals as shown in Table 9 were prepared as specimens (metal pieces to be treated), and the surfaces of the specimens were sequentially degreased and washed with water. A bath was then prepared that contained each metal surface treatment solution having each composition as shown in Table 9. Pure water was used as an aqueous medium of the metal surface treatment solution.

[0073] Next, each specimen was immersed while controlling the temperature of the metal surface treatment solution in the bath at each temperature as shown in Table 9. After immersion for each time as shown in Table 9, each specimen was taken out. Subsequently, the surface of each specimen was washed with water and then dried.

[Various Evaluations]

[0074] The specimens prepared in Examples 1 to 93 and Comparative Examples 1 to 10 were evaluated for a color tone and adhesion, as follows:

(Color Tone Evaluation)

[0075] The color tone of the surface of each specimen was visually evaluated. The evaluation criteria are shown below:

A: Antique gray having uniform and excellent treated appearance;
B: Antique gray darker than A, which has a uniform and excellent treated appearance;
C: Antique gray lighter than A, which has a uniform and excellent treated appearance; and
D: Not colored.

(Evaluation of Adhesion)

[0076] A cutting of 10 × 10 squares (100 squares in total) was created in the surface of each specimen with a cutter, and a number of squares was counted in which the colored coating did not peel off when a cellophane tape (registered trademark) was affixed and released. The size of one square was 1 mm × 1 mm in length × width.

[0077] In each table, the ratio is shown by (a number of squares where the colored coating did not peel off) / 100, which indicates that as the number of squares where the colored coating did not peel off is larger, the adhesion of the colored coating is higher.

[0078] Tables 1 to 9 show test conditions and evaluation results for Examples 1 to 93 and Comparative Examples 1 to 10.

[Table 1]

Example No	1	2	3	4	5
Colored Sample	A5052	A5052	A5052	A5052	A5052
Treatment Solution Composition	Na telluride 05g/L	Na telluride 1g/L	Na telluride 5g/L	Na telluride 50g/L	Na telluride 100g/L
	-	-	-	-	-
	-	-	-	-	-
	-	-	-	-	-
Temperature	80°C	60°C	50°C	40°C	20°C
Time	10 min	8 min	2 min	1 min	10 sec
pH	9	9	10	12	13
Color Tone	C	C	A	B	B
Adhesion	98/100	98/100	100/100	97/100	90/100
Example No	6	7	8	9	10
Colored Sample	A5052	A5052	A5052	A5052	A5052
Treatment Solution Composition	Na telluride 5g/L	Na telluride 5g/L	Na telluride 5g/L	Na telluride 5g/L	Na telluride 5g/L
	Na nitrate 1g/L	Na nitrate 10g/L	Na nitrate 20g/L	Na nitrate 150g/L	Na nitrate 200g/L
	-	-	-	-	-
	-	-	-	-	-
Temperature	50°C	50°C	40°C	40°C	30°C
Time	2 min	2 min	5 min	2 min	1 min
pH	10	10	10	10	10
Color Tone	A	A	A	B	B
Adhesion	97/100	97/100	100/100	98/100	95/100
Example No	11	12	13	14	15
Colored Sample	A5052	A5052	A5052	A5052	A5052
Treatment Solution Composition	Na telluride 5g/L	Na telluride 5g/L	Na telluride 5g/L	Na telluride 5g/L	Na telluride 5g/L
	Na sulfate 50g/L	Na sulfate 50g/L	Na sulfate 50g/L	Na sulfate 50g/L	Na sulfate 50g/L
	thiourea 0.1g/L	thiourea 1g/L	thiourea 10g/L	thiourea 30g/L	thiourea 50g/L
	-	-	-	-	-
Temperature	60°C	50°C	30°C	30°C	30°C
Time	2 min	2 min	2 min	30 sec	10 sec

(continued)

Example No	1	2	3	4	5
pH	10	10	10	10	10
Color Tone	B	B	B	B	C
Adhesion	91/100	95/100	97/100	95/100	90/100

[Table2]

Example No	16	17	18	19	20
Colored Sample	A5052	A5052	A5052	A5052	A5052
Treatment Solution Composition	Na telluride 5g/L	Na telluride 5g/L	Na telluride 5g/L	Na telluride 5g/L	Na telluride 5g/L
	Na sulfate 50g/L	Na sulfate 50g/L	Na sulfate 50g/L	Na sulfate 50g/L	Na sulfate 50g/L
	thiourea 10g/L	thiourea 10g/L	thiourea 10g/L	thiourea 10g/L	thiourea 10g/L
	citric acid 0.5g/L	citric acid 1g/L	citric acid 20g/L	citric acid 50g/L	citric acid 100g/L
	-	-	-	-	-
Temperature	20°C	30°C	30°C	40°C	40°C
Time	20 sec	1 min	2 min	5 min	10 min
pH	10	9	6	5	2
Color Tone	B	B	A	A	C
Adhesion	89/100	94/100	97/100	97/100	92/100
Example No.	21	22	23	24	25
Colored Sample	A5052	A5052	A5052	A5052	A5052
Treatment Solution Composition	Na telluride 5g/L	Na telluride 5g/L	Na telluride 5g/L	Na telluride 5g/L	Na telluride 5g/L
	Na sulfate 50g/L	Na sulfate 50g/L	Na sulfate 50g/L	Na sulfate 50g/L	Na sulfate 50g/L
	thiourea 10g/L	thiourea 10g/L	thiourea 10g/L	thiourea 10g/L	thiourea 10g/L
	Na citrate 20g/L	Na citrate 20g/L	Na citrate 20g/L	Na citrate 20g/L	Na citrate 20g/L
	Na chlorate 0.5g/L	Na chlorate 1g/L	Na chlorate 50g/L	Na chlorate 50g/L	Na chlorate 100g/L
Temperature	50°C	50°C	30°C	30°C	30°C
Time	2 min	1 min	2 min	2 min	1 min
pH	6	6	6	6	6
Color Tone	A	A	B	B	B
Adhesion	91/100	91/100	97/100	92/100	91/100
Example No.	26	27	28	29	30
Colored Sample	A5052	A5052	A5052	A5052	A5052

(continued)

Example No	16	17	18	19	20
Treatment Solution Composition	Na telluride 5g/L	Na telluride 5g/L	Na telluride 5g/L	Na telluride 5g/L	Na telluride 5g/L
	Na nitrate 20g/L	Na nitrate 20g/L	Na nitrate 20g/L	Na nitrate 20g/L	Na nitrate 20g/L
	-	-	-	-	-
	-	-	-	-	-
Temperature	10°C	30°C	40°C	60°C	80°C
Time	20 min	10 min	5 min	1 min	10 sec
pH	10	10	10	10	10
Color Tone	A	A	A	C	C
Adhesion	91/100	94/100	100/100	96/100	91/100

[Table 3]

Example No.	31	32	33	34	35
Colored Sample	ADC 12	ADC12	ADC12	ADC 12	ADC 12
Treatment Solution Composition	Na telluride 5g/L	Na telluride 5g/L	Na telluride 5g/L	Na telluride 5g/L	Na telluride 5g/L
	-	Na nitrate 20g/L	Na sulfate 50g/L	Na sulfate 50g/L	Na sulfate 50g/L
	-	-	thiourea 10g/L	thiourea 10g/L	thiourea 10g/L
	-	-	-	citric acid 20g/L	Na citrate 20g/L
	-	-	-	-	Na chlorate 50g/L
Temperature	50°C	40°C	30°C	30°C	30°C
Time	2 min	5 min	2 min	2 min	2 min
pH	10	10	10	6	6
Color Tone	A	A	B	A	B
Adhesion	89/100	94/100	100/100	90/100	97/100

[Table 4]

Example No.	36	37	38	39	40	41
Colored Sample	C2600P	C2600P	C2600P	C2600P	C2600P	C2600P

(continued)

Example No.	36	37	38	39	40	41
Treatment Solution Composition	telluric acid 0.5g/L	telluric acid 5g/L	telluric acid 100g/L	telluric acid 5g/L	telluric acid 5g/L	telluric acid 5g/L
	-	-	-	sulfuric acid 1g/L	sulfuric acid 100g/L	sulfuric acid 200g/L
	-	-	-	-		-
	-	-	-	-		-
Temperature	80°C	50°C	30°C	50°C	50°C	30°C
Time	20 min	10 min	1 min	10 min	2 min	2 min
pH	9	10	13	6	1 or less	1 or less
Color Tone	C	C	A	C	A	B
Adhesion	90/100	90/100	92/100	96/100	100/100	91/100
Example No	42	43	44	45	46	47
Colored Sample	C2600P	C2600P	C2600P	C2600P	C2600P	C2600P
Treatment Solution Composition	telluric acid 5g/L	telluric acid 5g/L	telluric acid 5g/L	telluric acid 5g/L	telluric acid 5g/L	telluric acid 5g/L
	sulfuric acid 50g/L	sulfuric acid 50g/L	sulfuric acid 50g/L	Na nitrate 50g/L	Na nitrate 50g/L	Na nitrate 50g/L
	thiodiglycol 0.1g/L	thiodiglycol 10g/L	thiodiglycol 50g/L	thiourea 5g/L	thiourea 5g/L	thiourea 5g/L
	-	-	-	citric acid 0.5g/L	citric acid 20g/L	citric acid 100g/L
Temperature	50°C	30°C	30°C	30°C	30°C	30°C
Time	2 min	2 min	30 sec	1 min	3 min	10 min
pH	1 or less	1 or less	1 or less	10	6	2
Color Tone	C	A	B	B	A	C
Adhesion	95/100	97/100	93/100	98/100	100/100	98/100

(continued)

Example No.	36	37	38	39	40	41
Example No	48	49	50			
Colored Sample	C2600P	C2600P	C2600P			
Treatment Solution Composition	telluric acid 5g/L	telluric acid 5g/L	telluric acid 5g/L			
	Na sulfate 50g/L	Na sulfate 50g/L	Na sulfate 50g/L			
	thiourea 10g/L	thiourea 10g/L	thiourea 10g/L			
	Na citrate 20g/L	Na citrate 20g/L	Na citrate 20g/L			
	boric acid 0.5g/L	boric acid 20g/L	boric acid 100g/L			
Temperature	30°C	30°C	30°C			
Time	2 min	2 min	2 min			
pH	6	5	4			
Color Tone	A	A	B			
Adhesion	90/100	98/100	91/100			

[Table 5]

Example No	51	52	53	54	55
Colored Sample	C1100P	C1100P	C1100P	C1100P	C1100P
Treatment Solution Composition	telluric acid 5g/L	telluric acid 5g/L	telluric acid 5g/L	telluric acid 5g/L	telluric acid 5g/L
	-	sulfuric acid 100g/L	sulfuric acid 50g/L	Na nitrate 50g/L	Na sulfate 50g/L
	-	-	thiodiglycol 10g/L	thiourea 5g/L	thiourea 10g/L
	-	-	-	citric acid 20g/L	Na citrate 20g/L
	-	-	-	-	boric acid 20g/L
Temperature	50°C	50°C	30°C	30°C	30°C
Time	10 min	5 min	2 min	3 min	2 min
nH	10	1 or less	1 or less	6	5
Color Tone	C	A	B	A	B
Adhesion	91/100	100/100	95/100	96/100	98/100

[Table 6]

Example No.	56	57	58	59	60	61
Colored Sample	ZDC2	ZDC2	ZDC2	ZDC2	ZDC2	ZDC2

(continued)

Example No.	56	57	58	59	60	61
Treatment Solution Composition	telluric acid 0.5g/L	telluric acid 5g/L	telluric acid 100g/L	telluric acid 5g/L	telluric acid 5g/L	telluric acid 5g/L
	-	-	-	hydrochloric acid 1g/L	hydrochloric acid 50g/L	hydrochloric acid 200g/L
	-	-	-	-	-	-
	-	-	-	-	-	-
	-	-	-	-	-	-
Temperature,	80°C	40°C	30°C	50°C	50°C	20°C
Time	10 min	1 min	30 sec	10 min	2 min	20 sec
pH	9	10	13	8	1 or less	1 or less
Color Tone	C	C	A	C	A	B
Adhesion	92/100	93/100	93/100	92/100	92/100	93/100
Example No.	62	63	64	65	66	67
Colored Sample	ZDC2	ZDC2	ZDC2	ZDC2	ZDC2	ZDC2
	telluric acid 5g/L	telluric acid 5g/L	telluric acid 5g/L	telluric acid 5g/L	telluric acid 5g/L	telluric acid 5g/L
Treat ment Solution Composition	sulfuric acid 50g/L	sulfuric acid 50g/L	sulfuric acid 50g/L	hydrochloric acid 50g/L	hydrochloric acid 50g/L	hydrochloric acid 50g/L
	thiourea 0.1g/L	thiourea 10g/L	thiourea 50g/L	thiourea 10g/L	thiourea 10g/L	thiourea 10g/L
	-	-	-	gluconic acid 0.5g/L	gluconic acid 20g/L	gluconic acid 100g/L
Temperature	80°C	50°C	30°C	50°C	50°C	70°C
Time	5 min	2 min	10 sec	2 min	2 min	5 min
pH	1 or less	1 or less	1 or less	9	5	3
Color Tone	A	B	B	B	A	C
Adhesion	95/100	97/100	92/100	91/100	100/100	92/100

(continued)

Example No.	56	57	58	59	60	61
Example No.	68	69	70			
Colored Sample	ZDC2	ZDC2	ZDC2			
Treatment Solution Composition	telluric acid 5g/L	telluric acid 5g/L	telluric acid 5g/L			
	Na phosphate 50g/L	Na phosphate 50g/L	Na phosphate 50g/L			
	thiourea 10g/L	thiourea 10g/L	thiourea 10g/L			
	gluconic acid 20g/L	gluconic acid 20g/L	gluconic acid 20g/L			
	Na chlorite 0.5g/L	Na chlorite 20g/L	Na chlorite 100g/L			
Temperatuee	50°C	50°C	50°C			
Time	2 min	2 min	2 min			
pH	6	9	12			
Color Tone	A	A	B			
Adhesion	98/100	99/100	93/100			

[Table 7]

Example No.	71	72	73	74	75
Colored Sample	Zinc Plating (Thickness on SPCC 8 μm)	Zinc Plating (Thickness on SPCC 8 μm)	Zinc Plating (Thickness on SPCC 8 μm)	Zinc Plating (Thickness on SPCC 8μm)	Zinc Plating (Thickness on SPCC 8μm)
Treatment Solution Composition	telluric acid 5g/L	telluric acid 5g/L	telluric acid 5g/L	telluric acid 5g/L	telluric acid 5g/L
	-	hydrochloric acid 50g/L	sulfuric acid 50g/L	Na sulfate 50g/L	Na phosphate 50g/L
	-	-	thiourea 10g/L	thiourea 10g/L	thiourea 10g/L
	-	-	-	gluconic acid 20g/L	gluconic acid 20g/L
	-	-	-	-	Na chlorite 20g/L
Temperature	40°C	50°C	50°C	50°C	40°C
Time	1 min	2 min	2 min	2 min	2 min
pH	10	1 or less	1 or less	5	9
Color Tone	C	B	B	A	B
Adhesion	92/100	92/100	97/100	98/100	99/100
Example No	76	77	78	79	80

(continued)

Example No.	71	72	73	74	75
Colored Sample	SPCC Sheet	SPCC Sheet	SPCC Sheet	SPCC Sheet	SPCC
Treatment Solution Composition	tellurium dioxide 5g/L	tellurium dioxide 5g/L	tellurium dioxide 5g/L	tellurium dioxide 5g/L	tellurium dioxide 5μ/L
	-	risodium phosphate	risodium phosphate 50g/	sulfuric acid 50g/L	sulfuric acid 50g/L
	-	-	thiocyanic acid 10g/L	thiocyanic acid 10g/L	thiourea 5g/L
	-	-	-	thylenediaminetetraacetic acid 20g/	citric acid 3g/L
	-	-	-	-	Na perchlorate 20g/L
Temperature	30°C	30°C	30°C	30°C	30°C
Time	2 min	2 min	2 min	2 min	3 min
pH	8	10	10	10	12
Color Tone	C	C	A	C	B
Adhesion	89/100	92/100	92/100	96/100	100/100

[Tabte 8]

Example No	81	82	83	84	85	86
Colored Sample				AZ31	AZ31	AZ91
Treatment Solution Composition	tellurium dioxide 5g/L	tellurium dioxide 5g/L	tellurium dioxide 5g/L	tellurium dioxide 5g/L	tellurium dioxide 5g/L	tellurium dioxide 5g/L
	-	nitric acid 50g/L	Na sulfate 50g/L	Na sulfate 50g/L	sulfuric acid 50g/L	sulfuric acid 50g/L
	-	-	thiourea 1g/L	thiocyanic acidk 10g/L	thiourea 5g/L	thiourea 5g/L
	-	-	-	Na carbonate 20g/L	citric acid 3g/L	citric acid 3g/L
	-	-	-	-	Na perchlorate 20g/L	Na perchlorate 20g/L
Temperature	30°C	30°C	30°C	30°C	50°C	50°C
Time	2 min	2 min	2 min	2 min	2 min	2 min
pH	8	1 or less	8	10	12	12
Color Tone	C	C	A	A	B	B
Adhesion	87/100	90/100	92/100	97/100	100/100	100/100

(continued)

Example No	81	82	83	84	85	86
Example No.	87	88	89	90	91	
Colored Sample	Ni200	Ni200	Ni200	Ni200	Ni200	
Treatment Solution Composition	Na telluride 5g/L	Na telluride 5g/L	Na telluride 5g/L	Na telluride 5g/L	Na telluride 5g/L	
	-	Na nitrate 20g/L	Na sulfate 50g/L	Na sulfate 50g/L	Na sulfate 50g/L	
	-	-	thiourea 10g/L	thiourea 10g/L	thiourea 10g/L	
	-	-	-	Na acetate 20g/L	Na acetate 20g/L	
	-	-	-	-	Na chlorate 50g/L	
Temperature	50°C	40°C	30°C	30°C	30°C	
Time	2 min	5 min	2 min	2 min	2 min	
pH	10	10	10	10	12	
Color Tone	C	C	B	A	B	
Adhesion	88/100	96/100	100/100	94/100	98/100	

Example No	92		93	
Step	Coloring	Coating	Coloring	Coating
Colored Sample	A5052	A5052	A5052	A5052
Treatment Solution Composition	Na telluride 5g/L	Stron JS Coat 200mL/L	Na telluride 5g/L	TR-170 200mL/L
	-	-	-	-
	-	-	-	-
	-	-	-	-
	-	-	-	-
Temperature	50°C	25°C	54°C	25°C
Time	2 min	30 sec	2 min	30 sec
pH	10	-	10	-
Color Tone	A	A	A	A
Adhesion	100/100	100/100	100/100	100/100

[Table 9]

Comp. No.	1	2	3	4		
Colored Sample	A5052	A5052	A5052	A5052		
Treatment Solution Composition	-	-	-	-		
	Na sulfate 50g/L	Na sulfate 50g/L	Na sulfate 50g/L	Na sulfate 50g/L		
	-	thiourea 10g/L	thiourea 10g/L	thiourea 10g/L		
	-	-	Na citrate 20g/L	Na citrate 20g/L		
	-	-	-	Na chlorate 50g/L		
Temperature	60°C	60°C	60°C	60°C		
Time	10 min	10 min	10 min	10 min		
pH	7	7	7	12		
Color Tone	D	D	D	D		
Adhesion	-	-	-	-		
Comp. No.	5	6	7	8	9	10
Colored Sample	C2600P	ZDC2	Zinc Plating (Thickness on SPCC 8μm)	SPCC	AZ31	Ni200
Treatment Solution Composition	-	-	-	-	-	-
	Na nitrate 50g/L	Na phosphate 50g/L	Na phosphate 50g/L	sulfuric acid 50g/L	sulfuric acid 50g/L	Na sulfate 50g/L
	thiourea 5g/L	thiourea 10g/L	thiourea 10g/L	thiourea 5g/L	thiourea 5g/L	thiourea 10g/L
	citric acid 20g/L	gluconic acid 20g/L	gluconic acid 20g/L	citric acid 3g/L	citric acid 3g/L	Na acetate 20g/L
	-	Na chlorite 20g/L	Na chlorite 20g/L	Na perchlorate 20g/L	Na perchlorate 20g/L	Na chlorate 50g/L
Temperature	60°C	60°C	60°C	60°C	60°C	60°C
Time	10 min	10 min	10 min	10 min	10 min	10 min
pH	4	12	12	6	6	6
Color Tone	D	D	D	D	D	D
Adhesion	-	-	-	-	-	-

[0079] It was confirmed from the above results that according to the metal surface treatment solution containing tellurium, the tellurium compound or the salt thereof as in Examples 1 to 93, the surface of the metal could be colored into the grayish color tone with good treatment efficiency.
On the other hand, it was confirmed that the metal surface could not be colored into the grayish color tone unless the metal surface treatment solution contained tellurium, the tellurium compound or the salt thereof, as can be seen from Comparative Examples 1 to 10.

Claims

1. A metal surface treatment solution, comprising tellurium, a tellurium compound, or a salt thereof.

2. The metal surface treatment solution according to claim 1, wherein the tellurium or the tellurium compound or the salt thereof is tellurium monoxide, tellurium dioxide, tellurium trioxide, tellurous acid, telluric acid, tellurium tetrachloride, dimethyl telluride, or a salt thereof, or a combination thereof.

3. The metal surface treatment solution according to claim 1 or 2, wherein a total content of the tellurium, the tellurium compound or the salt thereof is from 0.5 to 100 g/L.

4. The metal surface treatment solution according to any one of claims 1 to 3, further comprising an inorganic acid or a salt thereof.

5. The metal surface treatment solution according to claim 4, wherein the inorganic acid or the salt thereof is sulfuric acid, nitric acid, hydrochloric acid, phosphoric acid, or a salt thereof, or a combination thereof.

6. The metal surface treatment solution according to claim 4 or 5, wherein a total content of the inorganic acid or the salt thereof is from 1 to 200 g/L.

7. The metal surface treatment solution according to any one of claims 1 to 6, further comprising an organic sulfur compound or a salt thereof.

8. The metal surface treatment solution according to claim 7, wherein the organic sulfur compound or the salt thereof is thiourea, thiourea dioxide, thiodiglycol, dimethylthiourea, thiomalic acid, dithiodiglycolic acid, dimethylsulfoxide, methanesulfonic acid, p-toluenesulfonic acid, p-phenolsulfonic acid, thiocyanic acid, cysteine, methionine, or a salt thereof, or a combination thereof.

9. The metal surface treatment solution according to claim 7 or 8, wherein a total content of the organic sulfur compound or the salt thereof is from 0.1 to 50 g/L.

10. The metal surface treatment solution according to any one of claims 1 to 9, further comprising a carboxylic acid or a hydroxycarboxylic acid, or a salt thereof.

11. The metal surface treatment solution according to claim 10, wherein the carboxylic acid or the hydroxycarboxylic acid or the salt thereof is formic acid, acetic acid, propionic acid, lactic acid, malic acid, citric acid, oxalic acid, gluconic acid, malonic acid, succinic acid, benzoic acid, pyruvic acid, glyoxylic acid, nitrilotriacetic acid, ethylenediaminetetraacetic acid, or a salt thereof, or a combination thereof.

12. The metal surface treatment solution according to claim 10 or 11, wherein a total content of the carboxylic acid or the hydroxycarboxylic acid or the salt thereof is from 0.5 to 100 g/L.

13. The metal surface treatment solution according to any one of claims 1 to 12, further comprising an oxo acid or a salt thereof.

14. The metal surface treatment solution according to claim 13, wherein the oxo acid or the salt thereof is perchloric acid, chloric acid, chlorous acid, hypochlorous acid, bromic acid, carbonic acid, boric acid, or a salt thereof, or a combination thereof.

15. The metal surface treatment solution according to claim 13 or 14, wherein a total content of the oxo acid or the salt thereof is from 0.5 to 100 g/L.

16. The metal surface treatment solution according to any one of claims 1 to 15, wherein the metal to be treated is at least one selected from the group consisting of aluminum, aluminum alloys, copper, copper alloys, iron, iron alloys, zinc, zinc alloys, nickel, nickel alloys, magnesium, and magnesium alloys.

17. A metal surface treatment method, comprising a step of coloring a metal using the metal surface treatment solution according to any one of claims 1 to 16.

18. The metal surface treatment method according to claim 17, wherein, in the step of coloring the metal, the metal is immersed in the metal surface treatment solution at a temperature of from 10 °C to 80 °C for 10 seconds to 20 minutes to color the metal.

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EUROPEAN SEARCH REPORT

Application Number
EP 20 17 1700

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	EP 1 895 023 A1 (ARAI TAKASHI [JP]) 5 March 2008 (2008-03-05) * page 2, paragraph 4 - page 4, paragraph 17 * * page 4, paragraph 27; example 9 * * claims 1-9 * -----	1-12, 16-18	INV. C23C22/60 C23C22/62 C23C22/63 C23C22/64 C23C22/66
X	DE 21 50 143 A1 (CONS FOODS CORP) 7 December 1972 (1972-12-07) * the whole document * -----	1-7,9-18	
X	US 2 933 422 A (MASON WALTER A) 19 April 1960 (1960-04-19) * the whole document * -----	1-6,13, 15-17	
X	US 1 308 092 A (MATHERS FRANK C ET AL) 1 July 1919 (1919-07-01) * the whole document * -----	1,2,4,5, 17	
X	US 2 522 474 A (WAITKINS GEORGE R ET AL) 12 September 1950 (1950-09-12) * column 1, lines 1-9 * * column 1, line 20 - column 2, line 43 * * column 3, lines 23-27; examples 12-13:bath (f); table II * * examples I-III * -----	1-3,17	TECHNICAL FIELDS SEARCHED (IPC) C23C
X	EP 0 402 084 A1 (CALGON CORP [US]) 12 December 1990 (1990-12-12) * page 2, lines 3-41 * * page 3, line 45 - page 5, line 51 * * examples 1-5 * * claim 1 * ----- -/--	1-6, 10-17	

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
Munich	24 September 2020	Handrea-Haller, M

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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EUROPEAN SEARCH REPORT

Application Number
EP 20 17 1700

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	EP 0 536 993 A1 (CALGON CORP [US]) 14 April 1993 (1993-04-14) * page 2, lines 1-47 * * page 3, line 5 - page 6, line 9 * * page 6, lines 10-35; example example * * claims 1-8 * -----	1-6, 10-17	
			TECHNICAL FIELDS SEARCHED (IPC)

1

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	24 September 2020	Handrea-Haller, M

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