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(54) SURFACE-TREATED STEEL SHEET, ORGANIC RESIN-COATED STEEL SHEET, AND CONTAINER USING SAME

(57) [Problem] To provide a surface-treated steel sheet, etc. for which it is possible to restrain generation of sulfidation blackening while taking the influences of stannous oxide and stannic oxide into consideration.

[Solution] The surface-treated steel sheet of the present invention includes a steel sheet, a tin plating layer formed on the steel sheet, and a chemical conversion film that is formed on the tin plating layer and contains essentially no chromium. The surface-treated steel sheet is characterized in that in measurements using anode polarization, the current density ratio of a current density I1 at a potential representing a reaction of stannous oxide (SnO) after undergoing a heat treatment equivalent to coating and baking to the sum (I1 + I2), where 12 is a current density at a potential representing a reaction of stannic oxide (SnO2), is less than 0.36.

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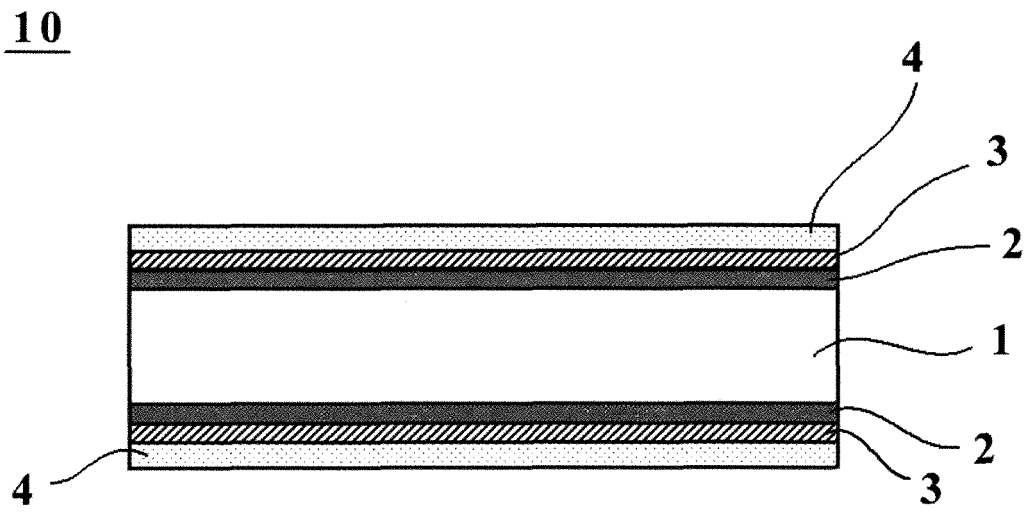
[Fig. 1]



Description

[Technical Field]

[0001] The present invention relates to a surface-treated steel sheet, an organic resin-coated steel sheet and a container, particularly to a surface-treated steel sheet, an organic resin-coated steel sheet and a container using the same which has undergone tin plating and for which generation of sulfidation blackening is restrained.

[Background Art]

[0002] In connection with steel sheets used in the fields of home electric appliances, construction materials, vehicles, airplanes, containers, and the like, the chromate treatment has been known as a treatment for enhancing the adhesion of the steel sheet to an organic resin formed on its surface, and has been widely used because of excellent corrosion resistance and adhesion thereof.

[0003] For tinplate (tin-plated steel sheet) and tin alloy-plated steel sheets used as containers such as beverage and food cans, for example, a chromate treatment in which a cathode electrolysis treatment is conducted in an aqueous solution of sodium dichromate is used. Since the surface of a tin-plated steel sheet or tin alloy-plated steel sheet having undergone such a chromate treatment has excellent adhesion to organic resins, a barrier layer of an organic resin can be favorably formed by coating, lamination, and the like.

[0004] Meanwhile, in the case where a container is filled with a food of high protein content such as fish meat, sulfidation blackening in which the container inner surface is blackened may be generated in a retort treatment step for high-temperature sterilization. This is considered to be the result of a process in which a sulfur-containing amino acid component such as cysteine and methionine in the fish meat is pyrolyzed, and H_2S or HS^- ion as the pyrolytic product reacts with tin and/or iron, to form a film of tin sulfide and/or iron sulfide in the container.

[0005] Note that a hydrous chromium oxide film (Cr^{OX}) formed by the chromate treatment has been able to produce a certain degree of restraining effect on also the above-mentioned sulfidation blackening.

[0006] However, although the above-mentioned chromate treatment is able to secure excellent corrosion resistance and adhesion, hexavalent chromium in the chromate treatment particularly has toxicity and exerts a high burden on the environment. In addition, to begin with, great expense is needed for waste water treatment, exhaust treatment, waste disposal, and the like, which are generated when the chromate treatment is conducted, irrespectively of the use of hexavalent chromium.

[0007] For this reason, in recent years, there is a strong trend toward a reduction, and finally abolition, of the use of chromium-containing compounds as well as hexavalent chromium, to begin with.

[0008] As a non-chromium surface treatment for substituting for the chromate treatment, there have been proposed a surface-treated steel sheet in which a film of aluminum oxide having corrosion resistance is formed on the surface of a steel sheet by a cathode electrolysis treatment using an electrolytic treatment liquid containing Al (aluminum) (PTL 1), and a surface-treated steel sheet based on the use of Al and a phosphoric acid compound film in combination (PTL 2 to 4).

[Citation List]

[Patent Literature]

[0009]

[PTL 1]
JP 2015-86439 A
[PTL 2]
WO 2016-121275
[PTL 3]
WO 2016-121276
[PTL 4]
WO 2016-121277

[Summary]

[Technical Problem]

[0010] However, while the technologies described in the above-mentioned PTL 1 to 4 can restrain the generation of

sulfidation blackening by use of a chromium-free chemical conversion film, there is yet room for improvement in the technologies, at least in the following points.

[0011] While some mentions of tin oxide are found in the above patent documents, tin oxides have been treated with generalization as SnO_X in the documents, and more detailed discussions on the influences of stannous oxide and stannic oxide have not been made yet.

[0012] The present invention has been made in consideration of solution to the above-mentioned problems. Accordingly, it is an object of the present invention to provide a surface-treated steel sheet, an organic resin-coated steel sheet, and a container using the same for which generation of sulfidation blackening can be restrained, while taking influences of stannous oxide and stannic oxide into account.

[Solution to Problem]

[0013] In order to solve the above-mentioned problem, according to an embodiment of the present invention, there is provided a surface-treated steel sheet which (1) includes: a steel sheet; a tin plating layer formed on the steel sheet; and a chemical conversion film that is formed on the tin plating layer and contains essentially no chromium, in which in measurements using anode polarization, a current density ratio of a current density I1 at a potential representing a reaction of stannous oxide (SnO) after undergoing a heat treatment equivalent to coating and baking to the sum (I1 + I2), where I2 is a current density at a potential representing a reaction of stannic oxide (SnO_2), is less than 0.36.

[0014] Further, in the surface-treated steel sheet as described in (1) above, (2) the chemical conversion film is preferably a film containing an aluminum-oxygen compound as a main ingredient.

[0015] Further, in the surface-treated steel sheet as described in (2) above, (3) the chemical conversion film preferably further contains a phosphoric acid compound.

[0016] Besides, in the surface-treated steel sheet as described in (1) above, (4) the chemical conversion film preferably contains zirconium.

[0017] In addition, in order to solve the above-mentioned problem, according to an embodiment of the present invention, there is provided an organic resin-coated steel sheet in which the surface-treated steel sheet according to any one of (1) to (4) above is coated with an organic resin.

[0018] Besides, in order to solve the above-mentioned problem, according to an embodiment of the present invention, there is provided a container including the surface-treated steel sheet according to any one of (1) to (4) above or the above-mentioned organic resin-coated steel sheet. Note that in such a container, the surface-treated steel sheet preferably has been subjected to coating and baking.

[Advantageous Effects of Invention]

[0019] According to the present invention, growth of stannous oxide which would cause sulfidation blackening can be restrained, and, therefore, starting points serving as generation sites of sulfidation blackening and spreading of the starting points can be restrained. Further, with stannic oxide also increased, the stannic oxide can produce an effect to function as a barrier layer for restraining reactions of the sulfur component with the surface-treated steel sheet.

[0020] In addition, where reactions of the tin oxide film (stannous oxide and stannic oxide) which would influence the generation of sulfidation blackening are measured by use of an electrochemical measurement device, it is thereby possible to easily predict the characteristic of sulfidation blackening resistance.

[Brief Description of Drawings]

[0021]

Fig. 1 is a sectional view illustrating schematically the structure of a surface-treated steel sheet according to the present embodiment.

Fig. 2 is a schematic diagram illustrating an example of anode polarization curves according to the present embodiment.

[Description of Embodiments]

<<Embodiment>>

[0022] An embodiment for carrying out the present invention will be described below.

[0023] A surface-treated steel sheet 10 according to the present embodiment illustrated in Fig. 1 includes a steel sheet 1 as a base material, a tin plating layer 2 formed on the steel sheet, and a chemical conversion film 3 that is formed on

the tin plating layer 2 and contains essentially no chromium (hereinafter, referred to as chromium-free film 3).

[0024] Note that while an example in which a film (the tin plating layer 2, the chromium-free film 3, or the like) is formed on both face-side and back-side surfaces of the steel sheet 1 will be described in the following embodiment, a film may be formed on only one surface of the steel sheet 1. In addition, in the present embodiment, a surface of the surface-treated steel sheet 10 may further be coated with an organic resin layer 4 to be an organic resin-coated steel sheet.

[0025] In the surface-treated steel sheet 10 of the present embodiment, in measurements using anode polarization, a current density ratio of a current density I1 at a potential representing a reaction of stannous oxide (SnO) to the sum (I1 + I2), where I2 is a current density at a potential representing a reaction of stannic oxide (SnO_2), is less than 0.36.

[0026] Each of components of the surface-treated steel sheet 10 according to the present embodiment will be described in detail below, referring to the drawings as required.

<Steel Sheet>

[0027] The steel sheet 1 as the base material need only be excellent in workability in drawing, workability in drawing and ironing, or workability in working (DTR) by drawing and unbending, and is not particularly limited. For example, a metal sheet of iron or any of various alloys or the like having a thickness of the order of 0.1 to 0.5 mm is used as the steel sheet 1.

[0028] For example, a hot rolled steel sheet using an aluminum-killed steel continuous cast material as a base, a cold rolled steel sheet obtained by cold rolling of the hot rolled steel sheet or the like can be used as the metal sheet. Note that a steel sheet obtained by pickling the aluminum-killed steel or the like by electrolytic pickling or the like to remove a scale on the surface, then cold rolling the steel sheet, and subjecting the steel sheet to electrolytic pickling, annealing, rolling, and the like, may be used as the cold rolled steel sheet.

<Tin Plating Layer>

[0029] The tin plating layer 2 of the present embodiment is formed, for example, on both sides of the steel sheet 1. The thickness of the tin plating layer 2 is not particularly limited, and need only be appropriately selected according to the use of the surface-treated steel sheet 10 to be manufactured. For example, the thickness in terms of tin amount is preferably not less than 0.5 g/m^2, more preferably from 1.0 to 15 g/m^2. Note that the tin plating layer 2 may be formed on at least one side of the steel sheet 1, as aforementioned.

[0030] The method for applying the tin plating layer 2 to the steel sheet 1 is not particularly limited, and examples of the method include methods using a known plating bath such as a ferrostan bath, a halogen bath, or a sulfate bath. Further, in the present embodiment, a tin-iron alloy layer may be formed between the steel sheet 1 and the tin plating layer 2 by a method in which after tin plating is conducted in the above-mentioned mode, a treatment (so-called reflow treatment) of heating to or above the melting temperature of tin and then quenching is conducted. When such a reflow treatment is performed, a tin-iron alloy layer is formed between the steel sheet 1 and the tin plating layer 2, whereby corrosion resistance is further enhanced.

[0031] As an example, a tin plating bath and its plating conditions will be set forth below.

[Tin plating bath and plating conditions]

[0032] Using a known ferrostan bath containing tin phenolsulfonate as a main ingredient, tin plating is formed on a steel sheet under the following conditions.

[0033] Bath temperature: 35 to 60°C
Stirring: as required
Cathode current: 1 to 20 A/dm^2
Anode material: known 99.999% metallic tin
Treatment time: five to 15 cycles, each cycle including a current passing time of one second and a stop time of 0.50 seconds
Reflow: direct current is passed to steel sheet 1 having tin plating layer 2 obtained, whereby steel sheet 1 is heated by heat generation due to electric resistance of base material to or above melting point of tin, followed by quenching with water
Note that while the ferrostan bath has been described as an example above, a halogen bath containing a tin halide as a main ingredient may be used.

<Chromium-free Film>

[0034] A chromium-free film 3 of the present embodiment is a chemical conversion film that is formed on the tin plating layer 2 and contains essentially no chromium. Note that the expression "contains essentially no chromium" in the present embodiment includes a case where the chemical conversion film would inevitably contain chromium as an impurity, in

addition to a mode in which the chemical conversion film does not contain any chromium component at all.

[0035] Besides, various chemical conversion films which contain essentially no chromium and in which in measurements using anode polarization described later, the current density ratio of a current density I1 at a potential representing a reaction of stannous oxide (SnO) to the sum (I1 + I2), where I2 is a current density at a potential representing a reaction of stannic oxide (SnO_2), is less than 0.36 can be applied as the chromium-free film 3 in the present embodiment. If the current density ratio exceeds 0.35, generation of sulfidation blackening would not be restrained, which is unfavorable.

[0036] Examples of such a chromium-free film 3 include a film containing a phosphoric acid compound, a film containing an aluminum-oxygen compound as a main ingredient, and a film containing zirconium.

[0037] Specific films preferable for the present embodiment will be described in detail below.

[Film that contains a phosphoric acid compound]

[0038] A phosphoric acid compound film as the chromium-free film 3 is a layer that contains tin phosphate, and is formed by immersing a steel sheet 1 formed with the aforementioned tin plating layer 2 (hereinafter referred to also as tin-plated steel sheet) in an electrolytic treatment liquid containing phosphoric acid ions, and performing a cathode electrolysis treatment with the steel sheet 1 side as a cathode.

[0039] In such an electrolytic treatment liquid, phosphoric acid (H_3PO_4), sodium dihydrogenphosphate (NaH_2PO_4), disodium hydrogenphosphate (Na_2HPO_4), phosphorous acid (H_3PO_3), and the like, can be used as a compound for forming phosphoric acid ions in the electrolytic treatment liquid. The phosphoric acid and phosphates may be used either singly or as a mixture thereof; among others, a mixture of phosphoric acid with sodium dihydrogenphosphate is preferred since it can cause favorable precipitation of tin phosphate as a phosphoric acid compound film.

[0040] In addition, the concentration of the phosphoric acid ions in the electrolytic treatment liquid is not particularly limited, and is preferably 5 to 200 g/L in terms of the amount of phosphorus. With the concentration of the phosphoric acid ions in the electrolytic treatment liquid set in the above-mentioned range, tin phosphate can be favorably precipitated on the tin-plated steel sheet.

[0041] Besides, the pH of the electrolytic treatment liquid is not specifically restricted, and is preferably 1 to 7. If the pH is less than 1, the formed tin phosphate would tend to be dissolved. On the other hand, if the pH exceeds 7, dissolution of an oxide film layer on the surface of the tin-plated steel sheet would be insufficient, resulting in that it may be impossible to form a homogeneous phosphoric acid compound film on the tin-plated steel sheet, since it is difficult to form a phosphoric acid compound film on the part where the oxide film layer is much left.

[0042] In addition, the temperature of the electrolytic treatment liquid is preferably 30 to 60°C.

[0043] In the present embodiment, a current is passed while the tin-plated steel sheet immersed in the electrolytic treatment liquid containing the phosphoric acid ions is set on the cathode side, whereby tin is dissolved from the tin-plated steel sheet, to generate tin ions (Sn^{2+}). The tin ions Sn^{2+} generated from the tin-plated steel sheet react with the phosphoric acid ions PO_4^{3-} in the electrolytic treatment liquid, resulting in precipitation as tin phosphate such as $Sn_3(PO_4)^2$ on the tin-plated steel sheet. In addition, the tin ions Sn^{2+} generated from the tin-plated steel sheet are precipitated also as tin oxide (SnO_X) on the tin-plated steel sheet.

[0044] The current density at the time of performing the cathode electrolysis treatment is not particularly limited, and is preferably 1 to 30 A/dm^2. With the current density set in the above-mentioned range, a phosphoric acid compound film can be favorably formed on the tin-plated steel sheet.

[0045] In this instance, the electrolytic quantity of electricity of the electrolytic treatment liquid is 1 to 10 C/dm^2, preferably 2 to 5 C/dm^2.

[0046] Besides, in subjecting the tin-plated steel sheet to the cathode electrolysis treatment, a counter electrode plate to be set against the tin-plated steel sheet may be any electrode plate that is not dissolved in the electrolytic treatment liquid during when the electrolytic treatment is conducted. From the viewpoint of being dissolved in the electrolytic treatment liquid with difficulty, however, a titanium plate coated with iridium oxide or a titanium plate coated with platinum is preferred.

[0047] In addition, the current passing time in performing the cathode electrolysis treatment is not specifically restricted, and is preferably 0.15 to 3.0 sec, more preferably 0.15 to 1.0 sec. It is necessary only to control the phosphorus content of the phosphoric acid compound film to an appropriate level, together with the current passing time.

[0048] The appropriate content of phosphorus in the phosphoric acid compound film is preferably 0.5 to 20 mg/m^2, more preferably 0.5 to 5.0 mg/m^2, and particularly preferably 0.9 to 4.0 mg/m^2.

[0049] Note that in regard of the aforementioned phosphoric acid compound film, the above-mentioned PTL 2 to 4, for example, may be further referred to. Besides, the phosphoric acid compound film is not indispensable as the chromium-free film 3, and it may be omitted as required.

[Film that contains an aluminum-oxygen compound as a main ingredient]

[0050] A film containing an aluminum-oxygen compound as a main ingredient (hereinafter referred to also as aluminum-oxygen compound film) as the chromium-free film 3 is formed on the tin plating layer 2 or on the phosphoric acid compound film. More specifically, for example, after washing the tin-plated steel sheet with water, the tin-plated steel sheet is subjected to an electrolytic treatment in an electrolytic treatment liquid that contains Al ions, whereby an aluminum-oxygen compound film can be precipitated on the tin-plated steel sheet. Note that specific examples of the aluminum-oxygen compound include Al_2O_3, $Al(OH)_3$, a composite oxide with fluorine represented by AlF_xO_y. In addition, as a compound for forming Al ions in the electrolytic treatment liquid, there can be used, for example, aluminum nitrate, aluminum sulfate, aluminum hydrochloride, aluminum fluoride, and the like. Where electrolysis is conducted in an electrolytic treatment liquid that contains fluorine, an Al compound film which contains fluorine and is composed mainly of aluminum and oxygen can be formed on the steel sheet 1 formed with the tin plating layer 2. Note that while fluorine is not indispensable but may be omitted as required, where the electrolytic treatment liquid contains F ions, the F ions function as a complexing agent for enhancing solubility of Al in the electrolytic treatment liquid.

[0051] The method for such an electrolytic treatment may be either of an anode electrolysis treatment and a cathode electrolysis treatment; from the viewpoint that an aluminum-oxygen compound film can be favorably formed, however, the cathode electrolysis treatment is preferred.

[0052] The content of Al ions in the electrolytic treatment liquid for forming the aluminum-oxygen compound film can be appropriately selected according to the film amount of the aluminum-oxygen compound film to be formed. The content of Al ions in the electrolytic treatment liquid, for example, in terms of mass concentration of Al atoms, is preferably 0.5 to 10 g/L, more preferably 1 to 5 g/L. Where the content of Al ions in the electrolytic treatment liquid is set in the above-mentioned range, stability of the electrolytic treatment liquid can be enhanced, and precipitation efficiency of the aluminum-oxygen compound can be enhanced.

[0053] Besides, at least one additive selected from among organic acids (citric acid, lactic acid, tartaric acid, glycolic acid, etc.), polyacrylic acid, polyitaconic acid, phenol resin, and the like, may be added to the electrolytic treatment liquid for forming the aluminum-oxygen compound film. Where these additives are appropriately added to the electrolytic treatment liquid either singly or in combination, an organic material can thereby be contained in the aluminum-oxygen compound film formed. This ensures that in the case of forming, for example, an organic resin layer 4 on the aluminum-oxygen compound film, the adhesion of the organic resin layer 4 can be enhanced.

[0054] In addition, in the case of forming the aluminum-oxygen compound film on the phosphoric acid compound film, it is desirable to control the content of phosphoric acid ions in the electrolytic treatment liquid for forming the aluminum-oxygen compound film. The content of the phosphoric acid ions in the electrolytic treatment liquid, in terms of the amount of phosphorus, is preferably not more than 0.55 g/L, more preferably not more than 0.33 g/L, and further preferably 0.11 g/L.

[0055] As a result, the aluminum-oxygen compound film is a uniform one, and the appearance quality of the surface-treated steel sheet 10 is enhanced.

[0056] Besides, at the time of forming the aluminum-oxygen compound film by the electrolytic treatment, it is preferable to use an intermittent electrolysis system in which a cycle of current passing and stopping of the current passing is repeated. In this instance, the total current passing time (the total current passing time in repeating the cycle of current passing and stopping of the current passing) for the base material is preferably not more than 1.5 sec, more preferably not more than one second. The number of cycles of the current passing and the stopping of the current passing is preferably one to 10, which may be controlled together with the current passing time in such a manner that the aluminum content of the aluminum-oxygen compound film will be suitable. Note that a suitable content of aluminum in the aluminum-oxygen compound film is preferably 3 to 40 mg/m^2, more preferably 5 to 15 mg/m^2, and particularly preferably 5.1 to 10.6 mg/m^2.

[0057] In addition, in forming the aluminum-oxygen compound film, a counter electrode plate disposed against the base material may be any electrode plate that is not dissolved in the electrolytic treatment liquid during when the electrolytic treatment is conducted. From the viewpoint of demonstrating a small oxygen overvoltage and being dissolved in the electrolytic treatment liquid with difficulty, however, a titanium plate coated with iridium oxide or a titanium plate coated with platinum is preferred.

[0058] Note that the pH of the electrolytic treatment liquid for forming the aluminum-oxygen compound film is preferably 1 to 5.

[0059] Besides, the temperature of the electrolytic treatment liquid for forming the aluminum-oxygen compound film is preferably 30 to 60°C.

[0060] Further, the electrolytic quantity of electricity in the electrolytic treatment liquid for forming the aluminum-oxygen compound film is 0.1 to 5 C/dm^2, preferably 0.2 to 1.6 C/dm^2.

[0061] Note that in regard of the aforementioned film that contains the aluminum-oxygen compound, the above-mentioned PTL 2 to 4, for example, may be further referred to.

[Film that contains zirconium]

[0062] A zirconium film as the chromium-free film 3 can be formed by subjecting the steel sheet 1 formed with the tin plating layer 2 to cathode electrolysis in an electrolytic treatment liquid which is an aqueous solution containing Zr ions and F ions. A chemical agent for forming Zr ions constituting the electrolytic treatment liquid is not particularly limited, and there can be used, for example, K_2ZrF_6, $(NH_4)_2ZrF_6$, $(NH_4)_2ZrO(CO_3)_2$, H_2ZrF_6, $ZrO(NO_3)_2$, $ZrO(CH_3COO)_2$, and the like. These chemicals may be used either singly or in combination of two or more of them.

[0063] As a result, a Zr compound film that contains fluorine and is composed mainly of zirconium and oxygen can be formed on the steel sheet 1 formed with the tin plating layer 2. Note that fluorine is not indispensable but may be omitted as required. However, where the electrolytic treatment liquid contains F ions, the F ions function as a complexing agent for enhancing solubility of Zr ions in the electrolytic treatment liquid, whereby a Zr compound film having a uniform film thickness can be precipitated.

[0064] The amount of Zr contained in the zirconium film is preferably in the range of 5 to 50 mg/m^2, more preferably 5 to 30 mg/m^2. On the other hand, in the case where the zirconium film contains fluorine, the amount of F is preferably in the range of 0.3 to 10 mg/m^2.

[0065] In addition, the Zr concentration in the electrolytic treatment liquid is preferably 1,000 to 10,000 ppm. Besides, the F concentration in the electrolytic treatment liquid is preferably 600 to 13,000 ppm.

[0066] In addition, the pH of the electrolytic treatment liquid for forming the zirconium film is preferably 2 to 5, and more preferably 2.5 to 4.

[0067] Besides, the temperature of the electrolytic treatment liquid is preferably 30 to 60°C.

[0068] In addition, a chemical agent for forming F ions contained in the electrolytic treatment liquid is not specifically restricted. There can be used, for example, ammonium zirconium fluoride, aluminum fluoride, titanium fluoride, sodium fluoride, ammonium fluoride, hydrofluoric acid, calcium fluoride, hexafluorosilicic acid, sodium hexafluorosilicate, and the like, among which chemical agents high in solubility in water are preferred.

[0069] Besides, the current density in the case of performing the electrolytic treatment is not particularly limited, and is preferably 1 to 30 A/dm^2.

[0070] In addition, in the case of forming the zirconium film by performing the cathode electrolysis treatment, a counter electrode plate may be any electrode plate that is not dissolved in the electrolytic treatment during when the cathode electrolysis treatment is conducted. From the viewpoint of demonstrating a small oxygen overvoltage and being dissolved in the electrolytic treatment liquid with difficulty, however, a titanium plate coated with iridium oxide is preferred.

[0071] Note that the zirconium film is not indispensable as the chromium-free film 3, but may be omitted as required.

<Organic Resin Layer>

[0072] The above-mentioned surface-treated steel sheet 10 may be formed further with an organic resin layer 4, to be an organic resin-coated steel sheet. Note that the organic resin layer 4 includes coating films of known coating materials or the like. Note that the organic resin layer 4 also may be formed on at least one side of the steel sheet 1, like the foregoing.

[0073] As a more specific example of the organic resin layer 4, there may be mentioned, for example, a thermoplastic resin. As the thermoplastic resin, there can be used olefin resin film of polyethylene, polypropylene, ethylene-propylene copolymer, ethylenevinyl acetate copolymer, ethylene-acrylate copolymer, ionomers, etc., polyester films of polyethylene terephthalate, polybutylene terephthalate, etc., unoriented or biaxially oriented films such as polyvinyl chloride film, polyvinylidene chloride film, etc., and polyamide films of nylon 6, nylon 6,6, nylon 11, nylon 12, etc. Among these, an unoriented polyethylene terephthalate obtained by copolymerization of isophthalic acid is particularly preferred. In addition, organic materials for constituting the organic resin layer may be used either singly or as a blend of different organic materials. Besides, a multilayer configuration including a plurality of organic resin layers may also be adopted. As a thermosetting resin, there can be used epoxy-phenolic resins, polyester resins, and the like.

[0074] Among these, polyester resins are preferable since they are easy to apply and bake, they are excellent in workability, adhesion to metal and retort resistance, and they do not generate a poisonous or corrosive gas when incinerated. Examples of such polyester resin include polyester resins containing at least one of ethylene terephthalate, butylene terephthalate, 1,4-cyclohexanedimethyl terephthalate, ethylene isophthalate, butylene isophthalate, ethylene adipate, butylene adipate, ethylene naphthalate, and butylene naphthalate.

<Container>

[0075] The surface-treated steel sheet 10 of the present embodiment can be formed as a container by a method in which, for example, the organic resin layer 4 is further formed thereon, to obtain an organic material-coated steel sheet, followed by working thereof.

[0076] Specific examples of such a container include seamless cans (two-piece cans) and three-piece cans (welded cans). Such a container can be manufactured by subjecting the organic material-coated steel sheet to conventionally known means such as, for example, drawing, drawing and re-drawing, bending and stretching by drawing and re-drawing, bending and stretching and ironing by drawing and re-drawing, or drawing and ironing.

<Current Density Ratio with Attention Paid to Stannous Oxide (SnO) and Stannic Oxide (SnO_2)>

[0077] The present inventors paid attention to the proportions of stannous oxide and stannic oxide, in regard of factors concerning the fact that a tinplate having undergone tin plating demonstrates excellent sulfidation blackening resistance. Specifically, the generation of tin sulfide (or iron sulfide) which causes the sulfidation blackening is considered to occur under an influence of the presence of stannous oxide on the surface of a tin-plated steel sheet (tinplate). It has been found that the amount of stannous oxide (SnO) increases when a heat treatment of coating and baking (approximately 150 to 210°C) is conducted in the process of can production, for example.

[0078] In addition, it has been found that while not only stannous oxide but also stannic oxide grows upon the heat treatment of coating and baking (approximately 150 to 210°C), stannous oxide serves as a starting point of generation of tin sulfide which causes sulfidation blackening, and, on the other hand, stannic oxide functions as a barrier layer for restraining the reaction between the above-mentioned sulfur component and the steel sheet side. It is to be noted, however, that the simple presence of a large amount of stannic oxide is not favorable and that excessive growth of stannic oxide would influence, for example, a lowering in adhesion of a coating material.

[0079] Therefore, even after undergoing the above-mentioned heat treatment, for example, if the surface-treated steel sheet 10 has a specific relation between stannous oxide and stannic oxide, generation of tin sulfide which causes sulfidation blackening can be restrained.

[0080] However, to determine the absolute amounts of stannous oxide and stannic oxide is technically very difficult at present, although investigations have been made by use of various techniques such as X-ray photoelectron spectroscopy, a glow discharge emission surface analyzer, and an X-ray diffraction method.

[0081] Under such findings, in the present embodiment, based on electrochemical measurement results utilizing anode polarization measurement, a ratio between stannous oxide and stannic oxide that is preferable for restraining the generation of tin sulfide or iron sulfide has been found. In other words, the present embodiment is characterized in that when a reaction due to anode polarization is utilized, the difference between a reaction of stannous oxide and a reaction of stannic oxide clearly appears as a potential difference, and stannous oxide and stannic oxide in the surface-treated steel sheet 10 can be discriminated from each other.

[0082] Where the chromium-free film 3 is formed on the tin plating layer 2 in such a manner that stannous oxide and stannic oxide satisfy this ratio, it is ensured that the growth of stannous oxide (SnO) after the heat treatment that would cause sulfidation blackening can be restrained.

[0083] Note that it is considered that the chromium-free film 3 described in the present embodiment is not in the form of being preferentially precipitated on the tin plating like a hydrous chromium oxide film conventionally used, but an amorphous film is precipitated in such a manner as to uniformly cover the whole part of the tin plating. It is considered, therefore, that where the chromium-free film 3 of the present embodiment is applied on the tin plating, the amount of SnO on the tin-plated steel sheet is reduced as a whole due to etching, electrolysis, or the like, whereby the number of active sites for SnS generation is decreased.

[0084] In addition, conventionally, a pretreatment step of immersion or an electrolytic treatment in an acidic or basic aqueous solution has been separately needed for reducing the amount of SnO in the tin plating layer, prior to chromate treatment. According to the present embodiment, however, the aforementioned strong etching action at the time of forming the chromium-free film 3 ensures that the same action as that of the pretreatment needed conventionally can be produced simultaneously with film formation. In other words, according to the present embodiment, the conventional pretreatment step is unnecessitated, and the production cost of the surface-treated steel sheet 10 can be suppressed.

<Electrochemical Measurement Method>

[0085] As an electrochemical measurement method, anode polarization measurement was used in the present embodiment. More specifically, the surface-treated steel sheet 10 as an object of measurement can be subjected to anode polarization measurement by use of a potentiostat device under the following conditions.

- Kind of model liquid: aqueous $Na_2S \cdot 9H_2O$ solution (containing 2 g/L of $Na_2S \cdot 9H_2O$)
- pH of liquid: 3 to 6
- Temperature of liquid: 30 to 50°C (preferably, 40 to 50°C)
- Measurement method

••Measurement area: 1 cm^2
••Polarization rate: 10 to 300 mV/min (preferably, 10 to 100 mV/min)

[0086] Note that the model liquid is not limited to sodium sulfide nonahydrate, and other corrosive solution such as aqueous sulfuric acid solution may be used. It is to be noted that attention should be paid to the fact that each potential (potential of SnO, SnO_2, and the like) of the film composition described later in the present embodiment is the value of the model liquid in the present embodiment. Since the value of each potential may vary if the model liquid is different, each potential required can be calculated by appropriate experiments or the like.

[0087] The measurement is performed by immersing the surface-treated steel sheet 10 in the model liquid. A potential is applied to the anode side from an immersion potential, and, while performing polarization at a polarization rate of 50 mV/min, current density is measured at predetermined time intervals.

[0088] Note that in order that the surface potential of the sample becomes stable, immersion potential may be measured in several tens of seconds (for example, 30 to 300 seconds), prior to anode polarization measurement, and thereafter the anode polarization measurement may be conducted.

[0089] Polarization curves (an example) based on the anode polarization measurement are illustrated in Fig. 2.

[0090] When samples having undergone the above-mentioned heat treatment are subjected to anode polarization in an aqueous $Na_2S{\cdot}9H_2O$ solution, two reactions, namely, a reaction of HS^- in the aqueous solution with SnO, SnO_2, and the like, and a reaction in which a metal is ionized and is converted into a sulfide are generated, as illustrated in Fig. 2.

[0091] Here, as the samples, (a) a tin-plated steel sheet formed with an Al film as a chromium-free film 3, (b) a tin-plated steel sheet not formed with the chromium-free film 3, and (c) a tin-plated steel sheet formed with a film by a chromate treatment, were used.

[0092] In addition, in Fig. 2, potentials of the film compositions that react with HS in the aqueous solution are indicated by arrows, and the relevant reactional formulas are represented by the following formulas. For example, the potential (-0.24 V) of SnO represents a fixed potential at which an oxidation-reduction reaction occurs in the aqueous $Na_2S{\cdot}9H_2O$ solution.

[0093] $Sn + H_2O \rightarrow SnO + 2H^+ + 2e^-$ (-0.24 V)
$SnO + H_2O \rightarrow SnO_2 + 2H^+ + 2e^-$ (-0.18 V)
$Fe \rightarrow Fe^{2+} + 2e^-$ ($Fe^{2+} + S^{2-} \rightarrow FeS$) (-0.1 V)
$Sn \rightarrow Sn^{2+} + 2e^-$ ($Sn^{2+} + S^{2-} \rightarrow SnS$) (0.38 V)

[0094] In the case of the surface-treated steel sheet 10 formed with the chromium-free film 3 (in this case, an aluminum film), the reaction with SnO is restrained, as compared to the case of other samples, and, further, the reactions with Fe, Sn and HS^- are also restrained. In other words, the chromium-free film 3 in the present embodiment can be not only restrained in its reaction with SnO, which is considered to be a starting point of generation of the sulfide, but also can be restrained in its reaction with Fe and Sn.

[0095] In addition, in the present embodiment, by electrochemically measuring the reaction of the tin oxide film which influences the generation of sulfidation blackening, the characteristics and generation of the sulfidation blackening can be predicted, which can be applied, for example, to selection of the kind, thickness, and the like, of the chromium-free film 3 to be coated with the tin plating layer 2 based on the measurement results.

<<Examples>>

[0096] The present invention will be described more in detail below by describing Examples.

<Example 1>

[0097] A cold rolled steel sheet of a low-carbon aluminum-killed steel having a thickness of 0.225 mm was used as the steel sheet 1 (base material). First, the steel sheet 1 was degreased by cathode electrolysis at 60°C for 10 seconds using an aqueous solution of a known alkali degreasing agent. The steel sheet 1 after degreasing was washed with tap water, and was pickled by immersing in a pickling treatment agent (5% aqueous sulfuric acid solution) at normal temperature for five seconds. Thereafter, the steel sheet 1 was washed with tap water, a tin plating layer 2 having a plating thickness of 2.8 g/m^2 was formed on the surface of the steel sheet using a known ferrostan bath under the following conditions, and, after washing with water, a reflow treatment was conducted, to produce a tin-plated steel sheet.

[Tin plating conditions]

[0098]

- Temperature: 40°C

- Stirring: as required
- Cathode current: 10 A/dm^2
- Anode current: 5 A/dm^2
- Anode material: commercial 99.999% metallic tin
- Treatment time: five to 15 cycles, each cycle including a current passing time of one second and a stop time of 0.50 seconds
- Reflow: direct current is passed to tin-plated steel sheet obtained, whereby steel sheet is heated by heat generation due to electric resistance of base material to or above melting point of tin, followed by quenching with tap water

[0099] On the tin-plated steel sheet obtained (the steel sheet 1 formed with the tin plating layer 2), a chromium-free film 3 (Al-oxygen compound film) was formed in a thickness of 16 mg/m^2 in the following procedure.

[0100] More specifically, the tin-plated steel sheet obtained was immersed in a treatment bath containing the ingredients of the following after-treatment composition liquid, and, while stirring the treatment bath, cathode electrolysis was conducted using as an anode an iridium oxide-coated titanium plate disposed at a position corresponding to an inter-electrode distance of 17 mm. Immediately after the cathode electrolysis, an after-treatment of washing with running water and drying was conducted.

[Electrolytic treatment liquid for Al treatment]

[0101]

- Composition of electrolytic treatment liquid: an aqueous solution having an Al concentration of 1,500 ppm by weight, a nitric acid ion concentration of 15,500 ppm by weight, and a total fluorine concentration of 0 ppm by weight, obtained by dissolving aluminum nitrate as an Al compound
- pH of electrolytic treatment liquid: 3.0
- Temperature of electrolytic treatment liquid: 40°C
- Electrolytic quantity of electricity: 1.6 C/dm^2

[Measurement of Al film amount]

[0102] The film amount of P and Al in the surface-treated steel sheet 10 obtained by forming the chromium-free film 3 (P and Al-oxygen compound film) was measured by a fluorescent X-ray device (produced by Rigaku Corporation; ZSX100e).

[Coating conditions]

[0103] Supposing a heat treatment of coating and baking (approximately 150 to 210°C) generated in the above-mentioned can production process or the like, the surface-treated steel sheet 10 obtained as above and subjected to a heat treatment at 190°C for 10 minutes was put to the following electrochemical measurement. Further, as a comparison, the surface-treated steel sheet not subjected to the heat treatment was also put to the following electrochemical measurement.

[0104] Note that such a heat treatment is conducted in a temperature range corresponding to the general coating and baking performed at the time of container production (can production or the like); for example, for the surface-treated steel sheet in the present embodiment, the heat treatment is conducted at approximately 150 to 210°C, as above-mentioned. However, the heat treatment corresponding to coating and baking is not limited to the above-mentioned temperature range, and a suitable temperature range may be appropriately set according, for example, to the material of the base material of the surface-treated steel sheet to be treated, the kind of plating, the film thickness of the plating, etc.

[Electrochemical measurement]

[0105] Anode polarization measurement was conducted using the above-mentioned potentiostat device. Note that an electrochemical measurement system HAG3001 produced by Hokuto Denko Corporation was used as the measurement device. In addition, an aqueous $Na_2S{\cdot}9H_2O$ solution (containing 2 g/L of $Na_2S{\cdot}9H_2O$ mixed therein) was used as the model liquid. Besides, the pH of the model liquid was 4.7, and the liquid temperature thereof was controlled to 37°C.

[0106] The measurement was conducted by immersing the surface-treated steel sheet 10 obtained as above in the model liquid. Note that in Example 1, in order that the surface potential of the sample becomes stable before anode polarization measurement, the anode polarization measurement was performed after preliminary measurement of immersion potential for 50 seconds. A potential was applied to the anode side from the immersion potential, and, while

performing polarization at a polarization rate of 50 mV/min, current density was measured at predetermined time intervals.

<Example 2>

[0107] Substantially the same procedure as in Example 1 was repeated, except that the electrolytic quantity of electricity in the electrolytic treatment liquid for Al treatment was 1.2 C/dm^2, and the thickness of the chromium-free film 3 (Al-oxygen compound film) was 10 mg/m^2.

<Example 3>

[0108] Substantially the same procedure as in Example 1 was repeated, except that the electrolytic quantity of electricity in the electrolytic treatment liquid for Al treatment was 0.8 C/dm^2, and the thickness of the chromium-free film 3 (Al-oxygen compound film) was 7 mg/m^2.

<Example 4>

[0109] Substantially the same procedure as in Example 1 was repeated, except that the electrolytic quantity of electricity in the electrolytic treatment liquid for Al treatment was 0.6 C/dm^2, and the thickness of the chromium-free film 3 (Al-oxygen compound film) was 5 mg/m^2.

<Example 5>

[0110] Substantially the same procedure as in Example 1 was repeated, except that a phosphoric acid compound film was formed before the Al treatment.

[0111] Specifically, first, a phosphoric acid compound film as a chromium-free film 3 (first chromium-free film) was formed on a tin-plated steel sheet. More specifically, the tin-plated steel sheet obtained as above-mentioned was immersed in the following electrolytic treatment liquid, and, while stirring the electrolytic treatment liquid, the phosphoric acid compound film was formed on the tin plating layer 2, using as an electrode an iridium oxide-coated titanium plate disposed at a position corresponding to an inter-electrode distance of 17 mm.

[0112] After the formation of the phosphoric acid compound film, an Al-oxygen compound film as a chromium-free film 3 (second chromium-free film) was formed in a thickness of 2 mg/m^2 in substantially the same manner as in Example 1.

[Electrolytic treatment liquid for P treatment]

[0113]

- Composition of electrolytic treatment liquid: an aqueous solution containing 10 g/L of phosphoric acid and 30 g/L of disodium hydrogenphosphate dissolved therein
- pH of electrolytic treatment liquid: 2.5
- Temperature of electrolytic treatment liquid: 40°C
- Electrolytic quantity of electricity: 3 C/dm^2

[Measurement of P film amount]

[0114] The film amounts of P and Al in the surface-treated steel sheet 10 obtained by forming the chromium-free films 3 (P and Al-oxygen compound films) were measured by a fluorescent X-ray device (produced by Rigaku Corporation; ZSX100e).

<Example 6>

[0115] Substantially the same procedure as in Example 5 was repeated, except that the electrolytic quantity of electricity in the electrolytic treatment liquid for Al treatment was 1.2 C/dm^2, and the thickness of the Al-oxygen compound film was 10 mg/m^2.

<Example 7>

[0116] Substantially the same procedure as in Example 5 was repeated, except that the electrolytic quantity of electricity in the electrolytic treatment liquid for Al treatment was 0.6 C/dm^2, and the thickness of the Al-oxygen compound film

was 5 mg/m^2.

<Example 8>

[0117] Substantially the same procedure as in Example 5 was repeated, except that the electrolytic quantity of electricity in the electrolytic treatment liquid for Al treatment was 0.4 C/dm^2, and the thickness of the Al-oxygen compound film was 3 mg/m^2.

<Example 9>

[0118] After a tin-plated steel sheet was obtained in substantially the same manner as in Example 1, a zirconium film (Zr^{ox}) as a chromium-free film was formed in a thickness of 10 mg/dm^2, by a method in which a treatment liquid obtained by dissolving ammonium zirconium fluoride as a zirconium ion source and having a Zr concentration of 5,500 ppm by weight and a pH of 3.0 was used at a treatment liquid temperature of 40°C and with an electrolytic quantity of electricity of 3 C/dm^2.

<Comparative Example 1>

[0119] After a tin-plated steel sheet was obtained in substantially the same manner as in Example 1, formation of the chromium-free film 3 was not conducted.

<Comparative Example 2>

[0120] Substantially the same procedure as in Example 1 was repeated, except that the electrolytic quantity of electricity in the electrolytic treatment liquid for Al treatment was 0.2 C/dm^2, and the thickness of the chromium-free film 3 (Al-oxygen compound film) was 2 mg/m^2.

<Comparative Example 3>

[0121] Substantially the same procedure as in Example 1 was repeated, except that the electrolytic quantity of electricity in the electrolytic treatment liquid for Al treatment was 0.4 C/dm^2, and the thickness of the chromium-free film 3 (Al-oxygen compound film) was 3 mg/m^2.

<Comparative Example 4>

[0122] Substantially the same procedure as in Example 5 was repeated, except that the electrolytic quantity of electricity in the electrolytic treatment liquid for Al treatment was 0.2 C/dm^2, and the thickness of the Al-oxygen compound film was 2 mg/m^2.

<Comparative Example 5>

[0123] Substantially the same procedure as in Example 5 was repeated, except that the electrolytic quantity of electricity in the electrolytic treatment liquid for P treatment was 4.2 C/dm^2, the electrolytic quantity of electricity in the electrolytic treatment liquid for Al treatment was 0.2 C/dm^2, and the thickness of the Al-oxygen compound film was 2 mg/m^2.

<Comparative Example 6>

[0124] After a tin-plated steel sheet was obtained in substantially the same manner as in Example 1, a zirconium film (Zr^{ox}) was formed in a thickness of 5 mg/dm^2, using substantially the same treatment liquid as in Example 9 and with an electrolytic quantity of electricity of 1.5 C/dm^2.

<Prior Art Example>

[0125] After a tin-plated steel sheet was obtained in substantially the same manner as in Example 1, a chromate treatment was conducted according to a conventional technique to form a hydrous chromium oxide film (Cr^{OX}) in a thickness of 6 mg/dm^2.

<Reference Example>

[0126] After a tin-plated steel sheet was obtained in substantially the same manner as in Example 1, a chromate treatment was conducted to form a laminate structure of metallic chromium (Cr^o) and a hydrous chromium oxide film (Cr^{OX}), with respective thicknesses of 10 mg/dm^2, and a total metallic Cr amount of 20 mg/dm^2.

[Evaluation of sulfidation blackening resistance]

[0127] The surface-treated steel sheet obtained in each of Examples and Comparative Examples was cut to 40 mm square, and the cut sections were protected with a 3 mm wide tape, to produce a specimen. Next, the thus produced specimen was put in a test container can (produced by Toyo Seikan Co., Ltd.; J280TULC), and the test container can was filled with the following model liquid for evaluation in such a manner that the specimen was wholly immersed. Thereafter, the test container can was seamed with an aluminum lid, and a retort treatment was conducted under the conditions of 130°C and five hours.

[0128] Thereafter, the test container can was opened, the degree of blackening of the specimen was observed by visual inspection, and evaluated according to the following criteria. Note that the evaluation of sulfidation blackening resistance evaluation was conducted with respect to all the Examples and Comparative Examples.

[0129]

- Model liquid for evaluation: An aqueous solution containing 3.0 g/L of sodium dihydrogenphosphate (NaH_2PO_4), 7.1 g/L of sodium hydrogenphosphate (Na_2HPO_4), and 6 g/L of L-cysteine hydrochloride monohydrate and having a pH of 7.0

[0130] Note that the evaluation of sulfidation blackening resistance is not limited to the case of using the above-mentioned model liquid for evaluation; for example, a real liquid present as a product in practice, such as salmon boiled plain, may also be used.

<<Evaluation Indexes>>

[0131]

○○: As a result of determination by visual inspection, the degree of blackening was apparently slighter as compared to Prior Art Example.
○: As a result of determination by visual inspection, the degree of blackening was substantially the same as compared to Prior Art Example.
×: As a result of determination by visual inspection, the degree of blackening was apparently heavier as compared to Prior Art Example.

[0132] Note that in evaluation, the sample with the evaluation index ○○ was judged to be applicable to practical use as a Cr-free type can material.

[0133] The specifications, the current density values obtained by anode polarization measurement, and the evaluation results of sulfidation blackening resistance with respect to Examples and Comparative Examples described above are set forth in Table 1.

[Table 1]

	Amount of Sn plating (g/m^2)	After-treatment (Film formed on tin plating layer)	Electrolytic treatment for forming phosphoric acid compound film		Electrolytic treatment for forming aluminum-oxygen compound film		Anode polarization curve Current density (mA/dm^2)		Anode polarization curve Current density (mA/dm^2)		Current density ratio	Current density ratio	Sulfidation blackening resistance
			Quantity of electricity (C/dm^2)	Amount of P after-treatment film (mg/m^2)	Quantity of electricity (C/dm^2)	Amount of Al after-treatment film (mg/m^2)	Heat treatment equivalent to coating, absent		Heat treatment equivalent to coating present		Heat treatment equivalent to coating absent	Heat treatment equivalent to coating, present	
							SnO(-0.24V) I1	SnO_2(-0.18V) I2	SnO(-0.24V) I1	SnO_2(-0.18V) I2	I1/(I1+I2)	I1/(I1+I2)	
Example 1	2.8g/m^2	Al treatment	-	-	1.6	16	0.010	0.050	0.012	0.050	0.167	0.194	○○
Example 2		Al treatment	-	-	1.2	10	0.013	0.050	0.014	0.040	0.206	0.259	○○
Example 3		Al treatment	-	-	0.8	7	0.024	0.080	0.018	0.060	0.231	0.231	○○
Example 4		Al treatment	-	-	0.6	5	0.030	0.140	0.033	0.060	0.176	0.355	○○
Example 5		P + Al treatment	3	2	1.6	16	0.038	0.080	0.008	0.070	0.322	0.103	○○
Example 6		P + Al treatment	3	2	1.2	10	0.060	0.130	0.000	0.090	0.316	0.000	○○
Example 7		P + Al treatment	3	2	0.6	5	0.120	0.240	0.010	0.080	0.333	0.111	○○
Example 8		P + Al treatment	3	2	0.4	3	0.220	0.310	0.014	0.080	0.415	0.149	○○
Example 9		Zr treatment	-	Zr^{ox}=10	-	-	0.030	0.100	0.230	0.120	0.231	0.343	○○
Comparative Example 1		Absent(only Sn plating)	-	-	-	-	0.350	0.550	0.260	0.100	0.389	0.722	×
Comparative Example 2		Al treatment	-	-	0.2	2	0.080	0.350	0.080	0.100	0.186	0.444	×
Comparative Example 3		Al treatment	-	-	0.4	3	0.046	0.180	0.041	0.070	0.204	0.369	○

(continued)

	Amount of Sn plating (g/m^2)	After-treatment (Film formed on tin plating layer)	Electrolytic treatment for forming phosphoric acid compound film		Electrolytic treatment for forming aluminum-oxygen compound film		Anode polarization curve Current density (mA/dm^2)		Anode polarization curve Current density (mA/dm^2)		Current density ratio	Current density ratio	Sulfidation blackening resistance
			Quantity of electricity (C/dm^2)	Amount of P after-treatment film (mg/m^2)	Quantity of electricity (C/dm^2)	Amount of Al after-treatment film (mg/m^2)	Heat treatment equivalent to coating, absent		Heat treatment equivalent to coating present		Heat treatment equivalent to coating absent	Heat treatment equivalent to coating, present	
							SnO(-0.24V) I1	SnO_2(-0.18V) I2	SnO(-0.24V) I1	SnO_2(-0.18V) I2	I1/(I1+I2)	I1/(I1+I2)	
Comparative Example 4		P + Al treatment	3	2	0.2	2	0.280	0.440	0.120	0.100	0.389	0.545	×
Comparative Example 5		P + Al treatment	42	2	0.2	2	0.330	0.400	0.160	0.100	0.452	0.615	×
Comparative Example 6		Zr treatment	-	Zr^{ox}=5	-	-	0.240	0.400	0.350	0.280	0.375	0.556	×
Prior Art Example		Chromate treatment	-	Cr^{ox}=6	-	-	0.025	0.015	0.050	0.090	0.625	0.357	○
Reference Example		Chromate treatment	-	Cr^{o}=10 Cr^{ox}=10	-	-	0.020	0.100	0.030	0.120	0200	0.250	○○

[0134] It was confirmed that in each of Examples, generation of tin sulfide which would cause sulfidation blackening was restrained, and excellent sulfidation blackening resistance was provided. On the other hand, it was confirmed that none of Comparative Examples had this characteristic.

[0135] In addition, in the chromate treatment which is a prior art technique, it was found that in order to obtain sulfidation blackening resistance equivalent to those in Examples, about three times more of the film amount was needed.

[0136] Note that in regard of the above-described Embodiment and Examples, various modifications are possible without departing from the scope of the gist of the present invention.

[Industrial Applicability]

[0137] As has been described above, the surface-treated steel sheet, the organic resin-coated steel sheet and the container using the same according to the present invention are sufficiently restrained from generation of sulfidation blackening, even in a situation of, for example, making contact with high protein, and are applicable to a wide field of industry.

[Reference Signs List]

[0138]

1 Steel sheet (base material)
2 Tin plating layer
3 Chromium-free film
4 Organic resin layer

Claims

1. A surface-treated steel sheet comprising:

a steel sheet;
a tin plating layer formed on the steel sheet; and
a chemical conversion film that is formed on the tin plating layer and contains essentially no chromium,
characterized in that in measurements using anode polarization, a current density ratio of a current density I1 at a potential representing a reaction of stannous oxide (SnO) after undergoing a heat treatment equivalent to coating and baking to the sum (I1 + I2), where 12 is a current density at a potential representing a reaction of stannic oxide (SnO_2), is less than 0.36.

2. The surface-treated steel sheet according to claim 1, wherein the chemical conversion film is a film containing an aluminum-oxygen compound as a main ingredient.

3. The surface-treated steel sheet according to claim 2, wherein the chemical conversion film further contains a phosphoric acid compound.

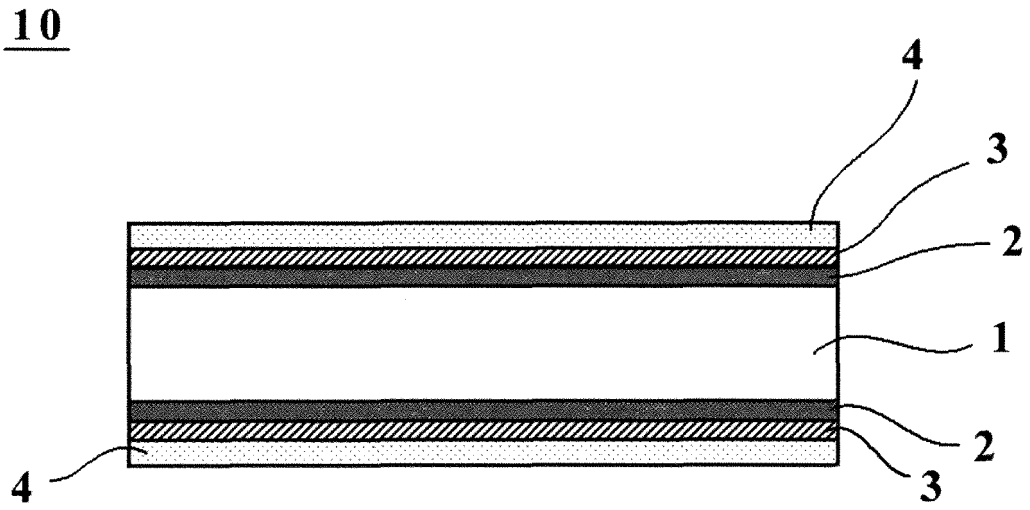
4. The surface-treated steel sheet according to claim 1, wherein the chemical conversion film contains zirconium.

5. An organic resin-coated steel sheet, wherein the surface-treated steel sheet according to any one of claims 1 to 4 is coated with an organic resin.

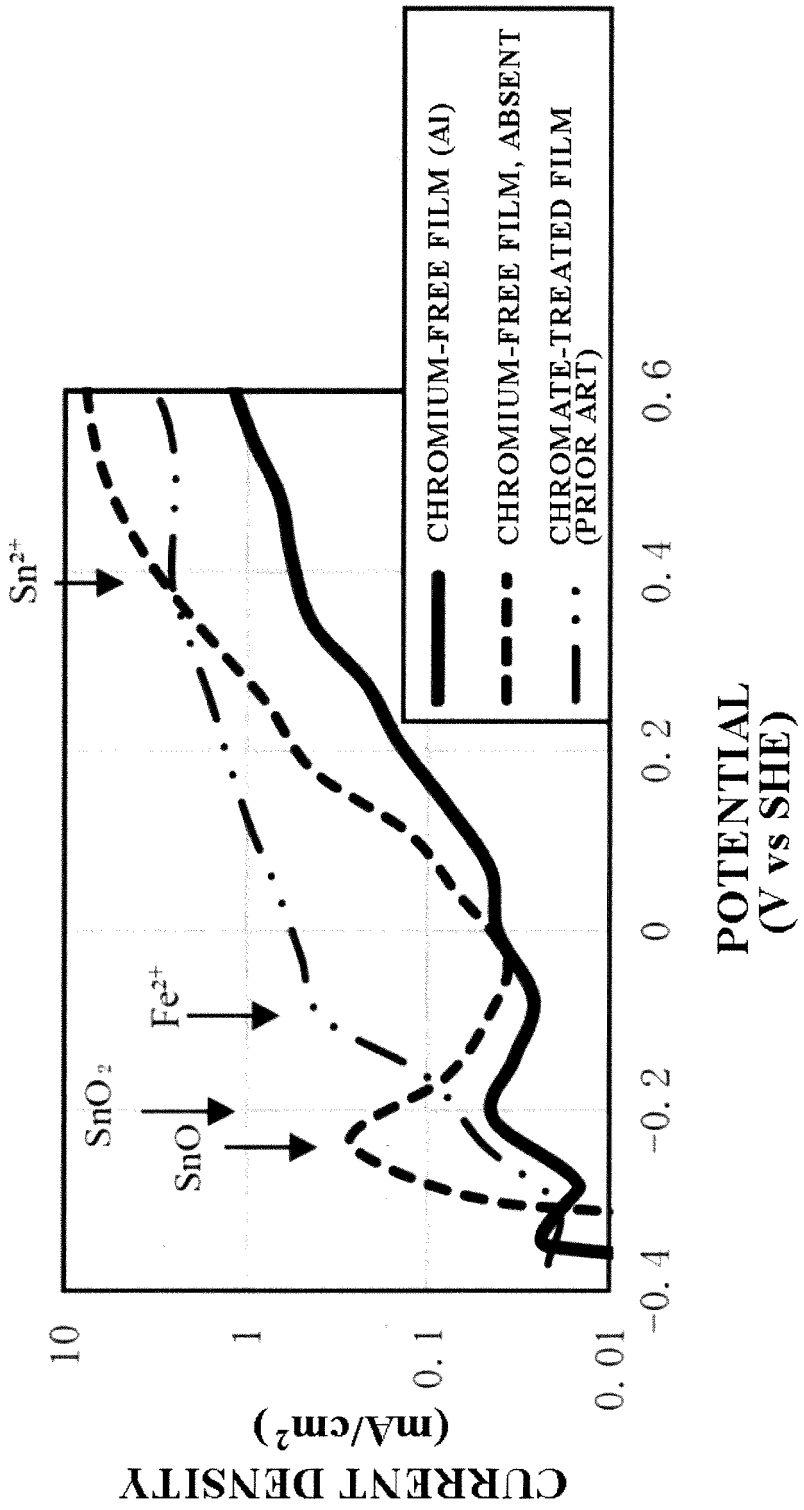
6. A container including the surface-treated steel sheet according to any one of claims 1 to 4 or the organic resin-coated steel sheet according to claim 5.

7. The container according to claim 6, wherein the surface-treated steel sheet has been subjected to coating and baking.

[Fig. 1]



[Fig. 2]


CHROMIUM-FREE FILM (Al)
CHROMIUM-FREE FILM, ABSENT
CHROMATE-TREATED FILM (PRIOR ART)
Sn2+
Fe2+
SnO2
SnO
10
1
0.1
0.01
−0.4
−0.2
0
0.2
0.4
0.6
CURRENT DENSITY (mA/cm2)
POTENTIAL (V vs SHE)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2017/027469

A. CLASSIFICATION OF SUBJECT MATTER
C23C28/00(2006.01)i, *B32B15/01*(2006.01)i, *B32B15/08*(2006.01)i, *B65D1/00*(2006.01)i, *B65D8/00*(2006.01)i, *C25D9/08*(2006.01)i

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)
C23C28/00, B32B15/01, B32B15/08, B65D1/00, B65D8/00, C25D9/08

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2017
Kokai Jitsuyo Shinan Koho 1971-2017 Toroku Jitsuyo Shinan Koho 1994-2017

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
JSTPlus/JMEDPlus/JST7580(JDreamIII)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	WO 2016/121275 A1 (Toyo Kohan Co., Ltd.), 04 August 2016 (04.08.2016), paragraphs [0001] to [0005]; paragraphs [0076] to [0084], example 1; tables 1 to 3; fig. 1 & TW 201641704 A	1-3,5-7 1-3,5-7
X Y	WO 2011/149047 A1 (Toyo Seikan Kaisha, Ltd.), 01 December 2011 (01.12.2011), claims 1, 10; paragraphs [0001] to [0007]; paragraph [0098], example 68; paragraph [0099], comparative example 17; tables 1, 7 & US 2013/0052478 A1 claims 1, 10; paragraphs [0001] to [0016]; paragraphs [0179] to [0181], example 68; comparative example 17; tables 1, 7 & CN 102918185 A	1,4-7 1,4-7

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

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
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"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
"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
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
22 August 2017 (22.08.17)	12 September 2017 (12.09.17)
Name and mailing address of the ISA/ Japan Patent Office 3-4-3,Kasumigaseki,Chiyoda-ku, Tokyo 100-8915,Japan	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2017/027469

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	Tsuneo INUI et al., "Mechanism of the Formation of Sulfide Stains on Tinplate", Journal of the Iron & Steel Institute of Japan, 1982, no.7, 1982, pages 850 to 857	1-7

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2015086439 A **[0009]**
- WO 2016121275 A **[0009]**
- WO 2016121276 A **[0009]**
- WO 2016121277 A **[0009]**