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(54) **METHOD FOR TREATING SURFACE OF ALUMINUM CAN**

(57) The purpose of the present invention is to provide a method for treating the surface of an aluminum can, in which an acidic treatment solution that is easy to handle can be used and the energy cost is sufficiently reduced. A method for treating the surface of an aluminum can, which comprises an alkali treatment step of treating the aluminum can with an alkaline treatment solution and an acid treatment step of treating the aluminum

can that has been subjected to the alkali treatment step with an acidic treatment solution, wherein the etching amount to be employed in the alkali treatment step is less than 50 mg/m². It is preferred that the alkaline treatment solution contains at least one ion selected from the group consisting of a sodium ion, a potassium ion and an ammonium ion.

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Description

TECHNICAL FIELD

5 **[0001]** The present invention relates to a method of treating the surface of an aluminum can.

BACKGROUND ART

10 **[0002]** Heretofore, aluminium cans such as beverage cans made of aluminum or an aluminium alloy are manufactured by a drawing process called the drawing and ironing process (hereafter referred to as the DI process). Aluminum powder (hereinafter referred to as smut) generated by scraping upon drawing and lubricating oil adhere to the surface of an aluminum cans which are manufactured by the DI process.

15 **[0003]** Usually, aluminum cans are subjected to chemical conversion treatment and paint treatment. In order to form a robust chemical conversion film and paint film, an oxide film formed on the surface of an aluminum can needs to be removed by etching after completely removing smut and lubricating oil adhering on the surface of the aluminum can before chemical conversion.

20 **[0004]** When performing surface treatment of an aluminum can, an acidic surface treatment liquid (hereinafter may be referred to as an acid treatment liquid) is commonly used, with which the surface of the aluminum can be moderately etched. For example, known is a method of treating the surface of an aluminum can with an acid treatment liquid containing trivalent iron ions in which pH is adjusted to 2 or less with sulfuric acid or nitric acid (for example, see Patent Documents 1 and 2). Also known is a method of treating the surface of an aluminum can with an acid treatment liquid containing organic sulfonic acid, trivalent iron ions and an inorganic acid such as sulfuric acid and nitric acid (for example, see Patent Document 3).

25 **[0005]** Note that for surface preparation of an aluminum for can tops instead of an aluminum can, known is a method including performing degreasing associated with etching by treating the surface of an aluminum for can tops made of a 5000-series alloy with an alkaline solution, and then performing acid wash (for example, see Patent Documents 4 to 6).

Patent Document 1: Japanese Examined Patent Application Publication No. H03-50838

Patent Document 2: Japanese Unexamined Patent Application, Publication No. 2000-104185

30 Patent Document 3: Japanese Unexamined Patent Application, Publication No. 2007-197775

Patent Document 4: Japanese Unexamined Patent Application, Publication No. 2003-119570

Patent Document 5: Japanese Unexamined Patent Application, Publication No. 2004-18992

Patent Document 6: Japanese Unexamined Patent Application, Publication No. 2008-127625

35 DISCLOSURE OF THE INVENTION

Problems to be Solved by the Invention

40 **[0006]** Meanwhile, in a case where impurities such as magnesium and copper remain on the surface of an aluminum can, a chemical film or a paint coating film may not be uniformly formed on the surface of the aluminum can, which in turn reduces the corrosion resistance of the aluminum can.

[0007] In order to avoid this, it is effective to increase the amount of etching by increasing the rate of etching with an acid treatment liquid. The amount of etching could be increased by increasing a temperature at which treatment is performed with an acid treatment liquid (for example, to 70°C). However, due to an increased energy cost, it is not preferred to maintain a temperature at which treatment is performed with an acid treatment liquid at a high temperature.

45 **[0008]** Patent Document 3 discloses that a temperature at which treatment is performed with an acid treatment liquid can be decreased by treating the surface of an aluminum can with an acid treatment liquid containing organic sulfonic acid. However, even in a case where the acid treatment liquid containing organic sulfonic acid is used, etching may not proceed sufficiently at a low temperature.

50 **[0009]** Note that acid wash is performed at a relatively low temperature (for example, at 50°C) in the surface preparation of an aluminum for can tops disclosed in Patent Documents 4 to 6. In the surface preparation of an aluminum for can tops, a substrate surface is etched by treatment with an alkaline solution performed before the acid wash. The acid wash in this case appears to be intended for removing magnesium segregated on an aluminum surface and for neutralizing an aluminum surface alkalinized by the treatment with an alkaline solution before the acid wash. As described above, 55 the purposes are completely different for the acid wash in the surface preparation of an aluminum for can tops, and for the treatment of etching a substrate surface with an acid treatment liquid performed in the surface treatment of an aluminum can. Suppose an aluminum can is treated under the conditions for the surface preparation of an aluminum for can tops, the amount of etching on the surface of an aluminum can would not be controlled, and thus a finishing

appearance of the aluminum can may not be controlled. Therefore, the technology for the surface preparation of an aluminum for can tops can not be applied to that for treating the surface of an aluminum can.

[0010] As described above, currently, a method of treating the surface of an aluminum can has not been found in which an acid treatment liquid with easy handling can be used, and the energy cost is sufficiently low.

[0011] The present invention is made in view of the above problems. An objective of the present invention is to provide a method of treating the surface of an aluminum can in which an acid treatment liquid with easy handling can be used, and the energy cost is sufficiently low.

Means for Solving the Problems

[0012] The present invention relates to a method of treating a surface of an aluminum can. The method includes: an alkaline treatment step of treating the aluminum can with an alkaline treatment liquid; and an acid treatment step of treating the aluminum can after the alkaline treatment step with an acid treatment liquid, in which the amount of etching in the alkaline treatment step is less than 50 mg/m².

[0013] The alkaline treatment liquid preferably contains at least one selected from the group consisting of sodium ions, potassium ions and ammonium ions.

[0014] It is preferable that the alkaline treatment liquid is at 40 to 70°C, and a treatment time of the aluminum can in the alkaline treatment step is 1 to 30 seconds.

[0015] The alkaline treatment liquid preferably contains at least one selected from the group consisting of an organic acid, a chelating agent, a dispersing agent and a surfactant.

[0016] It is preferable that the acid treatment liquid contains at least one selected from the group consisting of sulfuric acid, nitric acid and phosphoric acid, and contains 0.05 to 4 g/L of trivalent iron ions, and has a pH of 2 or less, and a treatment temperature of the aluminum can in the acid treatment step is 30 to 65°C.

[0017] A treatment time of the aluminum can in the acid treatment step is preferably 10 to 90 seconds.

[0018] The present invention relates to an aluminum can subjected to a surface treatment by the method of treating a surface of an aluminum can.

Effects of the Invention

[0019] The present invention can provide a method of treating the surface of an aluminum can in which an acid treatment liquid with easy handling can be used, and the energy cost is sufficiently low.

PREFERRED MODE FOR CARRYING OUT THE INVENTION

[0020] Below, embodiments of the present invention will be described. Note that the present invention shall not be limited to the following embodiments.

[0021] The method of treating the surface of an aluminum can according to the present invention (hereinafter also simply referred to as the surface treatment method) includes an alkaline treatment step and an acid treatment step. Aluminum cans to be treated by the surface treatment method according to the present embodiment include those made of a 3000-series alloy and the like.

<Alkaline treatment step>

[0022] In the alkaline treatment step, an aluminum can is treated with an alkaline treatment liquid.

[0023] The alkaline treatment liquid removes fat and oil components on the surface of an aluminum can. Further, in a case where an aluminum can after the DI process is treated, the alkaline treatment liquid also serves to remove a lubricant.

[0024] The amount of etching on the surface of an aluminum can in the alkaline treatment step is less than 50 mg/m². That is, the surface of an aluminum can hardly etched in the alkaline treatment step. In a case where the amount of etching in the alkaline treatment step is 50 mg/m² or more, etching is difficult to be controlled, resulting in whitening of the surface of an aluminum can. The amount of etching on the surface of an aluminum can in the alkaline treatment step can be calculated by measuring the mass of the aluminum can before and after the alkaline treatment step with a precision balance, and dividing the decrement in the mass of the aluminum can before and after the alkaline treatment step by the surface area of the aluminum can.

[0025] In order to achieve the amount of etching on the surface of an aluminum can of less than 50 mg/m² in the alkaline treatment step, it is necessary to control the pH of an alkaline treatment liquid, the concentration of an alkaline substance in the alkaline treatment liquid, the treatment time in the alkaline treatment step and the treatment temperature in the alkaline treatment step. More specifically, the amount of etching on the surface of an aluminum can can be

increased by increasing the concentration of an alkaline substance in the alkaline treatment liquid, i.e., increasing the pH of the alkaline treatment liquid, whereas the amount of etching can be decreased by decreasing it. Further, the amount of etching on the surface of an aluminum can can also be increased by increasing the treatment time in the alkaline treatment step or increasing the temperature of alkaline treatment whereas the amount of etching can be decreased by decreasing the treatment time or the treatment temperature. Note that all of these factors may not necessarily need to be adjusted, and an amount of etching on the surface of an aluminum can of less than 50 mg/m² may be achieved by adjusting only some of them.

[0026] The alkaline treatment liquid preferably has a pH of 9 to 14. A pH of the alkaline treatment liquid of 9 to 14 can allow a hydroxide film to form on the surface of an aluminum can. The hydroxide film formed on the surface of an aluminum can in the alkaline treatment step will be dissolved with an acid treatment liquid in the acid treatment step described below. In order to control the amount of etching while allowing a hydroxide film to efficiently form on the surface of an aluminum can in the alkaline treatment step, the pH of the alkaline treatment liquid is more preferably 10.0 to 13.0.

[0027] The alkaline treatment liquid preferably contains at least one selected from the group consisting of sodium ions, potassium ions and ammonium ions. These ions contained in the alkaline treatment liquid can form a hydroxide film effectively on the surface of an aluminum can. Sources of sodium ions, potassium ions and ammonium ions include inorganic substances such as sodium hydroxide, potassium hydroxide, sodium carbonate, sodium hydrogen carbonate and ammonium hydrogen carbonate; and organic substances such as sodium, potassium and ammonium salts of organic acids such as gluconic acid and citric acid. These compounds may be used in combination of two or more. The inorganic substances such as sodium hydroxide, which are alkaline, serve as sources of sodium ions, potassium ions or ammonium ions while they also can be sources of hydroxide ions.

[0028] The alkaline treatment liquid is preferably an aqueous solution containing sodium hydroxide. By using strongly basic aqueous sodium hydroxide as an alkaline treatment liquid, a hydroxide film can be formed more effectively on the surface of an aluminum can.

[0029] The concentration of an alkaline substance such as sodium hydroxide in the alkaline treatment liquid is preferably 0.01 to 10 g/L. When the concentration of an alkaline substance in the alkaline treatment liquid is less than 0.01 g/L, a hydroxide film tends not to be easily formed on the surface of an aluminum can. In contrast, when it is more than 10 g/L, whitening may occur due to excessive etching of the surface of an aluminum can.

[0030] Further, the alkaline treatment liquid preferably contains at least one selected from the group consisting of organic acids, chelating agents, dispersing agents and surfactants. In a case where the alkaline treatment liquid contains an organic acid, a chelating agent, a dispersing agent or a surfactant, smut on the surface of an aluminum can may efficiently be removed, and the formation of a hydroxide film can be promoted even if the alkaline treatment step is performed under mild conditions (for example, at low temperature, for short time).

[0031] Organic acids to be contained in the alkaline treatment liquid can include gluconic acid, citric acid, oxalic acid, malic acid, tartaric acid, sorbic acid, succinic acid and the like, and alkali metal salts such as sodium salts and potassium salts thereof. Among these, the alkaline treatment liquid more preferably contains at least one selected from the group consisting of gluconic acid, citric acid, oxalic acid, malic acid and tartaric acid.

[0032] Chelating agents to be contained in the alkaline treatment liquid can include aminocarboxylic acid-based chelating agents, phosphonic acid-based chelating agents and condensed phosphates. Specifically, they include ethylenediaminetetraacetic acid (EDTA), sodium 1-hydroxyethylidene-1,1-diphosphonate (HEDP), trisodium nitrilotriacetate (NTA), sodium tripolyphosphate (STPP) and the like. Among these, the alkaline treatment liquid more preferably contains at least one of ethylenediaminetetraacetic acid (EDTA) and sodium 1-hydroxyethylidene-1,1-diphosphonate (HEDP).

[0033] Dispersing agents to be contained in the alkaline treatment liquid can include acrylic acid-maleic acid copolymer and a sodium salt thereof, polycarboxylic acid, polyethylene glycol and the like. Among these, the alkaline treatment liquid more preferably contains acrylic acid-maleic acid copolymer.

[0034] For a surfactant to be contained in the alkaline treatment liquid, nonionic, cationic, anionic and zwitterionic surfactants can be used. Among these, nonionic systems are particularly preferred. For example, hydrocarbon derivatives, abietic acid derivatives, alcohol ethoxylate, denatured polyethoxylated alcohol and the like are preferably used.

[0035] Further, the alkaline treatment liquid more preferably contains at least one selected from the group consisting of organic acids, chelating agents and dispersing agents; and a surfactant. That is, preferred combinations of additives to be contained in the alkaline treatment liquid are combinations of at least one selected from the group consisting of organic acids, chelating agents and dispersing agents; and surfactants.

[0036] In a case where a combination of additives as described above are contained in the alkaline treatment liquid, both smut and lubricating oil on the surface of an aluminum can effectively be removed to further promote the formation of a hydroxide film even if the alkaline treatment step is performed under mild conditions (for example, at low temperature, for a short time) as described above. Therefore, in a case where the alkaline treatment liquid contains at least one selected from the group consisting of organic acids, chelating agents and dispersing agents; and a surfactant, consequently, desmutting of an aluminum can after the surface treatment can be further improved even if the alkaline treatment is performed under mild conditions.

[0037] The treatment time of an aluminum can in the alkaline treatment step is preferably 1 to 30 seconds. In a case where the treatment time of an aluminum can in the alkaline treatment step is shorter than 1 second, a hydroxide film tends not to be easily formed on the surface of the aluminum can. On the other hand, in a case where it is longer than 30 seconds, whitening of the surface of the aluminum can may occur due to excessive etching. The treatment time of an aluminum can in the alkaline treatment step is more preferably 3 to 20 seconds.

[0038] The treatment temperature of an aluminum can in the alkaline treatment step (the temperature of the alkaline treatment liquid) is preferably 40 to 70°C. In a case where the treatment temperature of an aluminum can in the alkaline treatment step is lower than 40°C, a hydroxide film tends not to be easily formed on the surface of the aluminum can. On the other hand, in a case where it is higher than 70°C, whitening of the surface of the aluminum can may occur due to excessive etching. The treatment temperature of an aluminum can in the alkaline treatment step is more preferably 45 to 60°C.

[0039] There is no particular limitation for methods of treating an aluminum can in the alkaline treatment step. Methods of treating an aluminum can in the alkaline treatment step include the spray method and the dipping method.

[0040] Treatment with the aforementioned alkaline treatment liquid may be performed once or multiple times in the alkaline treatment step.

[0041] In a case where treatment with the alkaline treatment liquid is performed multiple times in the alkaline treatment step, the treatment conditions (pH of the alkaline treatment liquid, treatment temperature, treatment time and the like) for each treatment may be the same or may be altered.

<Acid treatment step>

[0042] In the acid treatment step, the aluminum can after the alkaline treatment step is treated with an acid treatment liquid.

[0043] A hydroxide film is formed on the surface of an aluminum can without being passivated in the aforementioned alkaline treatment step. Since a hydroxide film is easily dissolved in an acid treatment liquid, the surface of an aluminum can be etched with a low-temperature acid treatment liquid in the acid treatment step. If the surface of an aluminum can were treated in the acid treatment step without performing the alkaline treatment step, the surface of the aluminum can would be passivated. Therefore, the temperature of the acid treatment liquid would need to be increased in order to facilitate etching. A high treatment temperature of an aluminum can (a high temperature of an acid treatment liquid) in the acid treatment step is not preferred because the energy cost in the surface treatment of an aluminum can is too high. In a case where the alkaline treatment step has been performed before the acid treatment step, the temperature of an acid treatment liquid can be lowered by 5 to 20°C as compared with the case where the alkaline treatment step has not been performed.

[0044] By making the acid treatment possible at low temperature in the acid treatment step, working environment can be improved, and further, a time required to re-start an aluminum-can processing line from the shutdown state can be shortened, leading to improved productivity. Moreover, acid corrosion of equipment can be slowed down, and thus the updating frequency of equipment can be reduced.

[0045] The acid treatment liquid preferably has a pH of 2 or less. When the pH of the acid treatment liquid is more than 2, etching of the surface of an aluminum can tends to be insufficient.

[0046] The acid treatment liquid preferably contains inorganic acid.

[0047] Inorganic acid will serve as an etching accelerator. Specific examples of inorganic acid include sulfuric acid, nitric acid and phosphoric acid, and these inorganic acids may be used alone or in combination. Note that sulfuric acid is more preferably used in view of being free of nitrogen and phosphorus.

[0048] The content of an inorganic acid in the acid treatment liquid is preferably 0.01 to 25 g/L. In a case where the content of an inorganic acid in the acid treatment liquid is less than 0.01 g/L, an etching rate is extremely low. On the other hand, in a case where it is more than 25 g/L, no further improvement is observed for the effect of etching, which is economically disadvantageous. The content of an inorganic acid in a more preferred acid treatment liquid is 0.5 to 20 g/L.

[0049] The acid treatment liquid preferably contains oxidized metal ions.

[0050] Usually, the etching reaction of aluminum in the acid treatment step includes an anode reaction in which aluminum becomes an aluminum ion (Al^{3+}) and a cathode reaction in which H^+ in the acid treatment liquid is reduced into $1/2 \text{H}_2$. For this reason, when oxidized metal ions such as ferric ions (Fe^{3+}) are added to the acid treatment liquid, an anode reaction in which the above Fe^{3+} is reduced into Fe^{2+} occurs simultaneously as the aforementioned reduction of H^+ , promoting the etching reaction of aluminum. Further, the adhesiveness of the metal with a chemical conversion film formed by chemical conversion after the acid treatment step is improved in a case where the acid treatment liquid contains oxidized metal ions.

[0051] In addition to ferric ions (Fe^{3+}), oxidized metal ions include metavanadic acid ions (VO^{3+}), ceric ions (Ce^{4+}), cobalt ions (Co^{5+}), stannic ions (Sn^{4+}) and the like.

[0052] According to the present embodiment, trivalent iron ions (ferric ions: Fe^{3+}) are preferably used as oxidized

metal ions. Oxidized metal ions are preferably supplied from water-soluble salts such as sulfate or nitrate. Therefore, trivalent iron ions are preferably supplied from ferric sulfate or ferric nitrate. Note that the concentration of ferrous ions (Fe^{2+}) increases as the etching reaction proceeds, and thus an oxidation-reduction potential (hereinafter, ORP) is decreased (also referred to as the aging of a cleaning agent), diminishing a promotion effect of etching an aluminum surface. Accordingly, an oxidizing agent for controlling ORP may be added as needed or at the beginning to oxidize ferrous ions into ferric ions. Oxidizing agents for controlling ORP at this time include hydrogen peroxide (H_2O_2), persulfates (for example, $\text{Na}_2\text{S}_2\text{O}_8^{2-}$), ozone (O_3), cerium compounds (for example, cerium ammonium sulfate: $(\text{NH}_4)_4\text{Ce}(\text{SO}_4)_4$), nitrites (for example, NaNO_2 , KNO_2) and the like. Note that metavanadate may be supplied as needed when metavanadic acid ions are used as oxidized metal ions.

[0053] The content of oxidized metal ions in the acid treatment liquid is preferably 0.05 to 4 g/L. In a case where the content of oxidized metal ions in the acid treatment liquid is less than 0.05 g/L, the amount of etching is insufficient, deteriorating desmutting properties. On the other hand, in a case where it is more than 4 g/L, no further improvement in detergency can be expected, representing an economical disadvantage. The content of oxidized metal ions in a more preferred acid treatment liquid is 0.1 to 1 g/L.

[0054] The acid treatment liquid preferably contains a surfactant.

[0055] Surfactants primarily serve to remove fat and oil components and lubricants remained on the surface of an aluminum can. They also serve to prevent removed fat and oil components and lubricant components from being suspended in a cleaning agent. That is, when fat and oil components and lubricant components are suspended in a cleaning agent, they may be re-adsorbed on the surface of an aluminum can. However, this problem can be avoided in a case where the acid treatment liquid contains a surfactant.

[0056] As a surfactant, nonionic, cationic, anionic and zwitterionic surfactants can be used. Among these, nonionic systems are particularly preferred, and for example, ethoxylated alkylphenol systems, hydrocarbon derivatives, abietic acid derivatives, primary ethoxylated alcohols, denatured polyethoxylated alcohols and the like are preferably used.

[0057] The content of a surfactant in the acid treatment liquid is preferably 0.01 to 10 g/L. In a case where the content of a surfactant in the acid treatment liquid is less than 0.01 g/L, detergency, in particular, a degreasing property is decreased. On the other hand, in a case where it is more than 10 g/L, the acid treatment agent may undergo foam formation, resulting in difficult treatment and further imposing a load on wastewater treatment. The content of a surfactant in a more preferred acid treatment liquid is 0.1 to 5 g/L.

[0058] The content of organic sulfonic acid in the acid treatment liquid is preferably 0.01 to 25 g/L. In a case where the content of organic sulfone in the acid treatment liquid is less than 0.01 g/L, a sufficient amount of etching may not be obtained. On the other hand, in a case where it is more than 25 g/L, the liquid stability of the acid treatment liquid tends to be decreased. In view of reducing a drain water load, the more preferred content of organic sulfonic acid in the acid treatment liquid is 0.1 to 5 g/L.

[0059] The amount of etching on the surface of an aluminum can in the acid treatment step is 60 to 100 mg/m^2 . In a case where the amount of etching in the acid treatment step is less than 60 mg/m^2 , etching is insufficient. Therefore, a chemical conversion film and a paint film described below tend not to be easily formed on the surface of an aluminum can. In a case where the amount of etching in the acid treatment step is more than 100 mg/m^2 , etching excessively proceeds. Therefore, whitening may occur on the surface of an aluminum can. The amount of etching on the surface of an aluminum can in the acid treatment step can be determined by measuring the mass of the aluminum can before and after the acid treatment step with a precision balance, and dividing the decrement in the mass of the aluminum can before and after the acid treatment step by the surface area of the aluminum can.

[0060] There is no particular limitation for methods of treating an aluminum can in the acid treatment step. Methods of treating an aluminum can in the acid treatment step include the spray method and the dipping method.

[0061] The treatment time of an aluminum can in the acid treatment step is preferably 10 to 90 seconds. In a case where the treatment time of an aluminum can in the acid treatment step is shorter than 10 seconds, etching on the surface of the aluminum can tends to be insufficient due to the too short treatment time. On the other hand, in a case where it is longer than 90 seconds, the surface of an aluminum can is excessively etched, resulting in a tendency of accelerated aging of an acid treatment agent. The treatment time of an aluminum can in the acid treatment step is more preferably 30 to 45 seconds.

[0062] The treatment temperature of an aluminum can in the acid treatment step is preferably 30 to 65°C. In a case where the treatment temperature of an aluminum can in the acid treatment step is lower than 30°C, the treatment temperature tends to be more difficult to be controlled. On the other hand, in a case where it is higher than 65°C, the energy cost tends to be increased. The treatment temperature of an aluminum can in the acid treatment step is more preferably 40 to 60°C.

<Chemical conversion and paint treatment>

[0063] The aluminum can after the acid treatment step is washed with water according to the conventionally known

method, and then subjected to a chemical conversion treatment with a phosphate-based or zircon-based chemical conversion liquid.

[0064] The aluminum can after the chemical conversion treatment is washed with water if necessary, and then subjected to paint treatment.

[0065] Smut and lubricating oil are removed from the aluminum can subjected to the surface treatment by the method of treating the surface of an aluminum can according to the present embodiment. Therefore, a robust chemical conversion film and paint film can be formed.

EXAMPLES

[0066] Next, the present invention is described in more detail based on Examples. However, the present invention shall not be limited to these. Note that the terms "part" and "%" are all based on mass unless otherwise stated.

<Example 1>

[0067] As an aluminum can, prepared was a lidless container having lubricating oil and smut adhered thereon, which was obtained by performing the DI process on a aluminum plate of a 3004 series alloy. The resulting material was subjected to a spray treatment at a treatment temperature of 40°C for 10 seconds using an alkaline treatment liquid adjusted to a pH of 12.5 with sodium hydroxide as an alkaline substance (the alkaline treatment). Subsequently, the aluminum can after the alkaline treatment was subjected to a spray treatment at a treatment temperature of 50°C for 40 seconds using an acid treatment liquid having 1 g/L of ferric ions and 2 g/L of a nonionic surfactant and adjusted to a pH of 1.0 with sulfuric acid as an acidic substance (the acid treatment). Note that the source of ferric ions for the acid treatment liquid is ferric sulfate.

[0068] Subsequently, washing was performed with tap water for 15 seconds, and then chemical conversion was further performed (at 40°C, for 12 seconds) with a chemical conversion agent ("Arusafu 450", Nippon Paint Co., Ltd.) under treatment conditions adjusted so that the amount of Zr in the film was 11 mg/m². After the chemical conversion, washing was performed with tap water for 15 seconds. Then spray washing was performed with deionized water for 5 seconds, and dried for 3 minutes at 195°C.

<Examples 2-26, Comparative Examples 1-15 and Reference Examples 1-3>

[0069] In the alkaline treatment step, the same aluminum can as used in Example 1 was subjected to a spray treatment with an alkaline treatment liquid adjusted to a pH shown in Tables 1 and 2 using an alkaline substance shown in Tables 1 and 2 at a treatment temperature and treatment time shown in Tables 1 and 2 (the alkaline treatment). In the acid treatment step, the aluminum can after the alkaline treatment was subjected to a spray treatment with an acid treatment liquid containing ferric ions, a nonionic surfactant and, if desired, organic sulfonic acid (HSO₃-CH₂CH(OH)CH₂OH) at concentrations shown in Tables 1 and 2 and adjusted to a pH shown in Tables 1 and 2 at a treatment temperature and treatment time shown in Tables 1 and 2 (the acid treatment).

[0070] Aluminum cans were treated as described above under the same conditions as in Example 1 except that the conditions were changed as shown in Tables 1 and 2.

[0071] Note that the mixture of sulfuric acid and nitric acid (the mass ratio: 10:1) were used as acidic substances for Example 21 and Comparative Example 11, the mixture of sulfuric acid and phosphoric acid (the mass ratio: 10:1) were used as acidic substances for Example 22 and Comparative Example 12, and the mixture of sulfuric acid and hydrofluoric acid (the mass ratio: 10:1) were used as acidic substances for Example 23 and Comparative Example 13, respectively.

[0072] Further, in Comparative Examples 5 to 15 and Reference Examples 1 to 3, the alkaline treatment step was not performed, but an aluminum can was washed at the same temperature as that of the acid treatment for 10 seconds using a liquid obtained by diluting the acid treatment liquid to be used in the next acid treatment step into a half of the concentration, and then subjected to the acid treatment step. Ferric ions were not contained in the acid treatment liquid for Example 23 and Comparative Examples 13, and a surfactant was not contained in the acid treatment liquid for Comparative Examples 3 and 6.

<Comparative Example 16>

[0073] In Comparative Example 16, the alkaline treatment step was not performed, but a spray treatment was performed at a treatment temperature of 60°C for 60 seconds with an alkaline degreasing liquid containing a surfactant and a chelating agent and adjusted to a pH of 12.5 using sodium hydroxide as an alkaline substance (the alkaline degreasing treatment). Subsequently, the aluminum can after the alkaline treatment was subjected to the acid treatment step performed under the conditions shown in Table 2.

[Table 1]

		Alkaline treatment conditions					Acid treatment conditions					Evaluation results					
		Alkaline substance	pH	Temperature (°C)	Time (seconds)	Amount of etching	Acidic substance (mass ratio)	Fe ³⁺ (g/L)	Surfactant (g/L)	Organic sulfonic acid (g/L)	pH	Time (seconds)	Temperature (°C)	Appearance	Water wettability	Desmutting properties	Corrosion resistance
Example	1	NaOH	10.5	40	10	A	Sulfuric acid	1	2	-	1.0	40	50	A	100	5	5
	2	NaOH	11.5	40	10	A	Sulfuric acid	1	2	-	1.0	40	50	A	100	5	5
	3	NaOH	12.5	40	10	A	Sulfuric acid	1	2	-	1.0	40	50	A	100	5	5
	4	NaOH	12.5	60	10	A	Sulfuric acid	1	2	-	1.0	40	50	A	100	5	5
	5	NaOH	12.5	60	5	A	Sulfuric acid	1	2	-	1.0	40	50	A	100	5	5
	6	NaOH	12.5	80	3	A	Sulfuric acid	1	2	-	1.0	40	50	A	100	5	5
	7	NaOH	12.5	40	5	A	Sulfuric acid	1	2	-	1.0	40	50	A	100	5	5
	8	NaOH	12.5	40	30	A	Sulfuric acid	1	2	-	1.0	40	50	A	100	5	5
	9	NH ₃	9.0	40	10	A	Sulfuric acid	1	2	-	1.0	40	50	A	100	4	5
	10	NH ₃	9.0	40	60	A	Sulfuric acid	1	2	-	1.0	40	50	A	100	5	5
	11	NH ₃	9.0	40	80	A	Sulfuric acid	1	2	-	1.0	40	50	A	100	5	5
	12	NH ₃	9.0	40	80	A	Sulfuric acid	1	0.1	-	1.0	40	50	A	100	5	5
	13	Na ₂ CO ₃	11.5	40	10	A	Sulfuric acid	1	2	-	1.0	40	50	A	100	5	5
	14	KOH	11.5	40	10	A	Sulfuric acid	1	2	-	1.0	40	50	A	100	5	5
	15	NaOH	13.5	40	10	A	Sulfuric acid	1	2	-	1.0	40	50	A	100	5	5
	16	NaOH	12.5	40	10	A	Sulfuric acid	1	2	-	0.5	40	50	A	100	5	5
	17	NaOH	12.5	40	10	A	Sulfuric acid	1	2	-	1.0	40	50	A	100	5	5
	18	NaOH	12.5	40	10	A	Sulfuric acid	1	2	-	2.0	40	50	A	100	5	5
	19	NaOH	12.5	40	10	A	Sulfuric acid	0.1	2	-	1.0	40	50	A	100	5	5
	20	NaOH	12.5	40	10	A	Sulfuric acid	3	2	-	1.0	40	50	A	100	5	5
	21	NaOH	12.5	40	10	A	Sulfuric acid/nitric acid (10/1)	1	2	-	1.0	40	50	A	100	5	5
	22	NaOH	12.5	40	10	A	Sulfuric acid/phosphoric acid (10/1)	1	2	-	1.0	40	50	A	100	5	5
	23	NaOH	12.5	40	10	A	Sulfuric acid/hydrofluoric acid (10/1)	-	2	-	1.0	40	30	A	100	5	5
	24	NaOH	12.5	40	10	A	Sulfuric acid	1	5	-	1.0	40	50	A	100	5	5
	25	NaOH	12.5	40	10	A	Sulfuric acid	1	2	1	1.0	40	40	A	100	5	5
	26	NaOH	12.5	40	10	A	Sulfuric acid	1	2	25	0.6	40	30	A	100	5	5

[Table 2]

	Alkaline treatment conditions						Acid treatment conditions						Evaluation results				
	Alkaline substance	pH	Temperature (°C)	Time (seconds)	Amount of etching	Acidic substance (mass ratio)	Fe ³⁺ (g/L)	Surfactant (g/L)	Organic sulfonic acid (g/L)	pH	Time (seconds)	Temperature (°C)	Appearance	Water wettability	Desmutting properties	Corrosion resistance	
Comparative Example	1	NaOH	12.5	80	10	B	Sulfuric acid	1	2	-	1.0	40	50	E	100	5	5
	2	NaOH	12.5	70	60	B	Sulfuric acid	1	2	-	1.0	40	50	E	100	5	5
	3	NaOH	12.5	80	80	B	Sulfuric acid	1	-	-	1.0	40	50	E	100	5	5
	4	NaOH	13.5	80	80	B	Sulfuric acid	1	2	-	1.0	40	50	E	100	5	5
	5	-	-	-	-	-	Sulfuric acid	1	2	-	1.0	40	50	C	90	3	2
	6	-	-	-	-	-	Sulfuric acid	1	-	-	1.0	40	50	C	80	3	2
	7	-	-	-	-	-	Sulfuric acid	1	2	-	0.5	40	50	B	100	4	3
	8	-	-	-	-	-	Sulfuric acid	1	2	-	2.0	40	50	D	80	3	2
	9	-	-	-	-	-	Sulfuric acid	0.1	2	-	1.0	40	50	C	90	3	2
	10	-	-	-	-	-	Sulfuric acid	3	2	-	1.0	40	50	B	100	4	4
	11	-	-	-	-	-	Sulfuric acid/nitric acid(10/1)	1	2	-	1.0	40	50	C	90	3	2
	12	-	-	-	-	-	Sulfuric acid/phosphoric acid (10/1)	1	2	-	1.0	40	50	C	90	3	2
	13	-	-	-	-	-	Sulfuric acid/hydrofluoric acid (10/1)	-	2	-	1.0	40	30	C	90	3	3
	14	-	-	-	-	-	Sulfuric acid	1	2	1	1.0	40	40	B	90	3	2
	15	-	-	-	-	-	Sulfuric acid	1	2	25	0.6	40	40	A	100	3	3
	16	Alkaline degreasing liquid	12.5	60	60	B	Sulfuric acid	-	-	-	3.5	5	50	E	100	3	3
Reference Example	1	-	-	-	-	-	Sulfuric acid	1	2	-	1.0	40	70	A	100	5	5
	2	-	-	-	-	-	Sulfuric acid	1	2	1	1.0	40	60	A	100	5	5
	3	-	-	-	-	-	Sulfuric acid	1	2	25	0.6	40	40	A	100	5	5

<Examples 27-44 and Comparative Example 17>

[0074] In the alkaline treatment step, the same aluminum can as used in Example 1 was subjected to a spray treatment at a treatment temperature and treating time shown in Table 3 with an alkaline treatment liquid containing an organic acid, a chelating agent, a dispersing agent and a surfactant at concentrations shown in Table 3 and adjusted to a pH shown in Table 3 using an alkaline substance shown in Table 3 (the alkaline treatment). In the acid treatment step, the aluminum can after the alkaline treatment was subjected to a spray treatment at a treatment temperature and treatment time shown in Table 3 with an acid treatment liquid containing ferric ions and a nonionic surfactant at concentrations shown in Table 3 and adjusted to a pH shown in Table 3 (the acid treatment).

[0075] Aluminum cans were treated as described above under the same conditions as in Example 1 except that the conditions were changed as shown in Table 3. Note that in a case where a surfactant was contained in the alkaline treatment liquid, 2 g/L of a nonionic surfactant was contained. Further, the acrylic acid-maleic acid copolymer used in Example 35 is SOKALAN CP5 from Basf Japan.

[0076] Further, in Comparative Example 17, the alkaline treatment step was not performed, but the same aluminum can as used in Example 1 was subjected to a spray treatment at a treatment temperature and treatment time shown in Table 3 with an acidic solution containing 0.5 g/L of citric acid. Then, in the acid treatment step, the aluminum can was subjected to a spray treatment at a treatment temperature and treatment time shown in Table 3 with an acid treatment liquid containing ferric ions and a nonionic surfactant at concentrations shown in Table 3 and adjusted to a pH shown in Table 3.

[Table 3]

Table 3

Table 3	Example	Alkaline treatment conditions										Acid treatment conditions							Evaluation results			
		Alkaline substance	Organic acid		Chelating agent, Dispersing agent	Content (g/L)	Surfactant (g/L)	pH	Temperature (°C)	Time (seconds)	Amount of etching	Acidic substance	Fe ³⁺ (g/L)	Surfactant (g/L)	Organic sulfonic acid (g/L)	pH	Time (seconds)	Temperature (°C)	Appearance	Water wettability	Desmutting properties	Corrosion resistance
			Species	Content (g/L)																		
	27	NaOH	-	-	-	-	10.5	40	5	A	Sulfuric acid	1	2	-	1.0	40	50	A	100	4	5	
	28	NaOH	Gluconic acid	0.5	-	-	10.5	40	5	A	Sulfuric acid	1	2	-	1.0	40	50	A	100	5	5	
	29	NaOH	Citric acid	0.5	-	-	10.5	40	5	A	Sulfuric acid	1	2	-	1.0	40	50	A	100	5	5	
	30	NaOH	Oxalic acid	0.5	-	-	10.5	40	5	A	Sulfuric acid	1	2	-	1.0	40	50	A	100	5	5	
	31	NaOH	Malic acid	0.5	-	-	10.5	40	5	A	Sulfuric acid	1	2	-	1.0	40	50	A	100	5	5	
	32	NaOH	Tartaric acid	0.5	-	-	10.5	40	5	A	Sulfuric acid	1	2	-	1.0	40	50	A	100	5	5	
	33	NaOH	-	-	HEDP	0.5	10.5	40	5	A	Sulfuric acid	1	2	-	1.0	40	50	A	100	5	5	
	34	NaOH	-	-	EDTA	0.5	10.5	40	5	A	Sulfuric acid	1	2	-	1.0	40	50	A	100	5	5	
	35	NaOH	-	-	Acrylic acid-maleic acid copolymer	0.5	10.5	40	5	A	Sulfuric acid	1	2	-	1.0	40	50	A	100	5	5	
	36	NaOH	Gluconic acid	0.5	-	-	10.5	40	5	A	Sulfuric acid	1	2	-	1.0	40	50	A	100	5	5	
	37	NaOH	Sodium gluconate	0.5	-	-	10.5	40	5	A	Sulfuric acid	1	2	-	1.0	40	50	A	100	5	5	
	38	NaOH	Potassium citrate	1	-	-	10.5	40	5	A	Sulfuric acid	1	2	-	1.0	40	50	A	100	5	5	
	39	NaOH	Sodium citrate	1	-	-	10.5	40	5	A	Sulfuric acid	1	2	-	1.0	40	50	A	100	5	5	
	40	NaOH	-	-	-	0.5	10.5	40	5	A	Sulfuric acid	1	2	-	1.0	40	50	A	100	5	5	
	41	NaOH	-	-	-	3	10.5	40	5	A	Sulfuric acid	1	2	-	1.0	40	50	A	100	5	5	
	42	NaOH	Gluconic acid	0.5	-	-	0.5	10	40	2	A	Sulfuric acid	1	2	-	1.0	40	50	A	100	5	5
	43	NaOH	Citric acid	0.5	-	-	0.5	10	40	2	A	Sulfuric acid	1	2	-	1.0	40	50	A	100	5	5
	44	NaOH	Gluconic acid	0.5	EDTA	0.5	3	10	40	2	A	Sulfuric acid	1	2	-	1.0	40	50	A	100	5	5
Comparative Example	17	-	Citric acid	0.5	-	-	-	3.3	40	5	A	Sulfuric acid	1	2	-	1.0	40	50	B	100	4	4

[Evaluation]

(a) Amount of etching

5 **[0077]** The mass of an aluminum can before and after the alkaline treatment step was measured with a precision balance. The decrement in the mass of the aluminum can before and after the alkaline treatment step was divided by the surface area of the aluminum can. The resulting value was taken as the amount of etching, which was evaluated into the following 2 categories. Results are shown in Tables 1, 2 and 3.

10 A: less than 50 mg/m²
B: 50 to 100 mg/m²

(b) Appearance

15 **[0078]** Whiteness inside the container after drying was visually evaluated. Those having a white appearance which were fully degreased and desmuted and sufficiently etched were considered as Good, and evaluated into the following 5 categories depending on whiteness. Results are shown in Tables 1, 2 and 3.

20 A: Entirely white
B: Partly light gray
C: Overall light gray
D: Partly gray
E: Entirely gray

25 (c) Water wettability

[0079] The container immediately after spray wash with water after the chemical conversion was shaken 3 times to drain off water, and allowed to stand upward for 30 seconds. The water stained area (%) of the outer surface of the container was then measured. Results are shown in Tables 1, 2 and 3.

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(d) Desmutting properties

35 **[0080]** Transparent adhesive tapes were made adhered on the surfaces of the aluminum cans after the surface treatment obtained from the present Examples, Comparative Examples and Reference Examples. Next, they were removed, and then attached on white mount paper to compare the whiteness of the surfaces of the attached tapes with other parts of the white mount paper. Those in which smut was completely removed without contamination were considered as Good, and evaluated into the following 5 categories depending on the degree of contamination. Results are shown in Tables 1, 2 and 3. 5: No contamination

40 4: Trace level of Contamination
3: Low level of contamination
2: Moderate level of Contamination
1: Significant level of contamination

45 (e) Resistance to boiling-water blackening (corrosion resistance)

[0081] Appearance evaluation was performed according to the following criteria after immersing the aluminum cans after the surface treatment obtained from the present Examples, Comparative Examples and Reference Examples in boiling water for 30 minutes. Results are shown in Tables 1, 2 and 3.

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5: No change in appearance
4: Partly slight blackening
3: Overall slight blackening
2: Partly dark blackening
55 1: Overall blackening

[0082] As clearly understand from comparison and the like of Examples 1 to 11, 13 to 15 and 17 with Comparative Example 5, good results for the appearance, the water wettability, the degree of desmutting, and the resistance to boiling-

water blackening (corrosion resistance) of an aluminum can can not be obtained in a case where the acid treatment is performed without the alkaline treatment, as compared with the case where an aluminum can is subjected to the acid treatment after the alkaline treatment. The above results appear to be caused because the surface of an aluminum can is not sufficiently etched in the acid treatment step in a case where the alkaline treatment has not been performed. Note that as shown in Reference Example 2, the surface of an aluminum can can be sufficiently etched when the temperature of the acid treatment is increased even in a case where the acid treatment is performed without performing the alkaline treatment. Therefore, the surface of an aluminum can excellent in the appearance, the water wettability, the degree of desmutting and the resistance to boiling-water blackening (corrosion resistance) can be obtained.

[0083] When Examples 1 to 11, 13 to 15 and 17 are compared with Reference Example 1, good evaluation results are obtained in Examples 1 to 11, 13 to 15 and 17 as well as in Reference Example 1 while the treatment temperatures in the acid treatment step of Examples 1 to 11, 13 to 15 and 17 are lower by 20°C than that in Reference Example 1. Therefore, it was possible to decrease the temperature of the acid treatment step by 20°C when the alkaline treatment step was first performed prior to the acid treatment step.

[0084] Further, as clearly shown from comparison of Examples 25 and 26 with Comparative Examples 14 and 15, satisfactory evaluation results can not be obtained in particular for the degree of desmutting and the resistance to boiling-water blackening (corrosion resistance) in a case where the alkaline treatment is not performed even if organic sulfonic acid is contained in the acid treatment liquid. Note that in a case where organic sulfonic acid is contained in an excessive amount, waste fluid treatment of the acid treatment liquid tends to be complicated.

[0085] Further, when Example 25 is compared with Reference Example 2, good evaluation results are obtained for Example 25 as well as in Reference Example 2 while the treatment temperature of the acid treatment step is lower by 20°C than that of Reference Example 2. Therefore, even in a case where the acid treatment liquid contained organic sulfonic acid, it was possible to decrease the temperature of the acid treatment step by 20°C when the alkaline treatment step was first performed prior to the acid treatment step.

[0086] Further, when Example 26 is compared with Reference Example 3, good evaluation results are obtained for Example 26 as well as in Reference Example 3 while the treatment temperature of the acid treatment step is lower by 10°C than that of Reference Example 1. Therefore, even in a case where the acid treatment liquid contained a large amount of organic sulfonic acid (25 g/L), it was possible to decrease the temperature of the acid treatment step by 10°C when the alkaline treatment step was first performed prior to the acid treatment step.

[0087] Further, even in a case where the alkaline treatment step was performed prior to the acid treatment step as in Comparative Examples 1 to 4, the appearance of an aluminum can was found to deteriorate, resulting in overall graying when the amount of etching was 50 mg/m² or more in the alkaline treatment step. The above results appear to be caused because etching control is difficult when the amount of etching is increased in the alkaline treatment step.

[0088] Further, as in Comparative Example 16, in a case where etching was sufficiently proceeded in the alkaline degreasing step prior to the acid treatment step as in the surface preparation of aluminum for can tops, the appearance of an aluminum can was found to deteriorate, resulting in overall graying.

[0089] Further, as clearly understand by comparing Example 27 with Examples 28 to 44, desmutting of the surface treated aluminum can was found to be better when an organic acid, a chelating agent, a dispersing agent or a surfactant was contained in the alkaline treatment liquid as compared with the case where these were not contained even though the alkaline treatment step was performed under mild conditions (for short time). The above results are likely to be caused because smut on the surface of an aluminum can is efficiently removed in a case where the alkaline treatment liquid contains an organic acid, a chelating agent or a dispersing agent, leading to facilitation in the formation of a hydroxide film. Further, in a case where the alkaline treatment liquid contains a surfactant, lubricating oil on the surface of an aluminum can is efficiently removed, and this likely leads to facilitation in the formation of a hydroxide film.

Claims

1. A method of treating a surface of an aluminum can, comprising:

an alkaline treatment step of treating the aluminum can with an alkaline treatment liquid, and
an acid treatment step of treating the aluminum can after the alkaline treatment step with an acid treatment liquid,

wherein an amount of etching in the alkaline treatment step is less than 50 mg/m².

2. The method of treating a surface of an aluminum can according to claim 1, wherein the alkaline treatment liquid contains at least one selected from a group consisting of sodium ions, potassium ions and ammonium ions.

3. The method of treating a surface of an aluminum can according to claim 1 or 2, wherein the alkaline treatment liquid is at 40 to 70°C, and a treatment time of the aluminum can in the alkaline treatment step is 1 to 30 seconds.
- 5 4. The method of treating a surface of an aluminum can according to any one of claims 1 to 3, wherein the alkaline treatment liquid contains at least one selected from a group consisting of organic acid, a chelating agent, a dispersing agent and a surfactant.
- 10 5. The method of treating a surface of an aluminum can according to any one of claims 1 to 4, wherein the acid treatment liquid contains at least one selected from a group consisting of sulfuric acid, nitric acid and phosphoric acid, and contains 0.05 to 4 g/L of trivalent iron ions, and has a pH of 2 or less, and a treatment temperature of the aluminum can in the acid treatment step is 30 to 65°C.
- 15 6. The method of treating a surface of an aluminum can according to any one of claims 1 to 5, wherein a treatment time of the aluminum can in the acid treatment step is 10 to 90 seconds.
7. An aluminum can subjected to a surface treatment by the method of treating a surface of an aluminum can according to any one of claims 1 to 6.

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INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

C23G1/22(2006.01)i, C11D3/04(2006.01)i, C11D3/20(2006.01)i, C11D7/04
(2006.01)i, C11D7/26(2006.01)i, C23G1/12(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)

C23G1/22, C11D3/04, C11D3/20, C11D7/04, C11D7/26, C23G1/12

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 1996-2014
Kokai Jitsuyo Shinan Koho 1971-2014 Toroku Jitsuyo Shinan Koho 1994-2014

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2000-309839 A (The Furukawa Electric Co., Ltd.), 07 November 2000 (07.11.2000), entire text (Family: none)	1-7
A	JP 5-239434 A (Nihon Parkerizing Co., Ltd.), 17 September 1993 (17.09.1993), entire text & EP 413328 A1 & KR 10-1996-0014931 B & US 5030323 A & US 5064500 A & WO 1995/002660 A1 & WO 1996/009363 A1 & WO 1996/019553 A1	1-7

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