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(71) Applicant: **Nippon Paint Co., Ltd.**
Osaka-shi, Osaka 531-0077 (JP)

(72) Inventors:
- **Ikeda, Satoshi**
  Yamato-shi, Kanagawa 242-0021 (JP)
- **Kamimura, Masayuki**
  Ichikawa-shi, Chiba 272-0025 (JP)
- **Sonomura, Kazuo**
  Katsushika-ku, Tokyo 125-0041 (JP)

(74) Representative:
Forstmeyer, Dietmar, Dr. rer. nat., Dipl.-Chem.
Boeters & Bauer,
Bereiteranger 15
81541 München (DE)

(54) Pickling kit for aluminum substrates and method of pickling

(57) The present invention provides a pickling method for aluminum substrate

which comprises supplementing, in the course of pickling of an aluminum substrate, a pickling agent with a solution (A) and a solution (B)
to thereby uphold the formulated components within the above concentration ranges,
said pickling agent containing 3000 to 50000 ppm of sulfuric acid, 100 to 5000 ppm of a surfactant, 50 to 3000 ppm of an oxidized metal ion or anion and 100 to 5000 ppm of nitric acid,
said solution (A) containing 30 to 500 mass parts of sulfuric acid, 1 to 50 mass parts of a surfactant, 0.5 to 30 mass parts of an oxidized metal ion or anion and 30 to 500 parts of water, and
said solution (B) containing 0.5 to 30 mass parts of nitric acid, 0.5 to 30 mass parts of an oxidizing agent and 10 to 300 mass parts of water.

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Description

FIELD OF THE INVENTION

[0001] The present invention relates to a pickling kit suited to the degreasing and desmutting of aluminum articles such as aluminum can bodies and to an associated pickling method.

PRIOR ART

[0002] The surface of an aluminum article, such as a beverage can, just as formed from aluminum or alloyed aluminum has been covered with aluminum oxide and oil. The aluminum can, ih particular, is usually fabricated by the drawing technique called "drawing and ironing (DI)" and the surface of the can produced by this technique has deposits of the fine aluminum shavings (smut) generated on drawing and the lubricating oil used. Therefore, in order that an intimate chemical conversion film and/or a coating film may be formed on such an aluminum substrate, its surface must be cleaned beforehand by removing the aluminum oxide film or smut and oil.

[0003] The surface cleaning of an aluminum article is generally made using a chromate type, hydrofluoride type, chromium-free type or fluorine-free type pickling agent which etches off the metallic surface in a suitable degree. Generally, the etching reaction of aluminum which takes place in such an acidic cleaning agent comprises an anodic reaction by which aluminum is converted to aluminum ion (Al^{3+}) and a cathodic reaction by which H^+ in the agent is reduced to 1/2 H_2. Therefore, when a oxidized metal ion or oxoanion (hereinafter sometimes referred to briefly as "oxidized ion"), for example a ferric ion (Fe^{3+}), is added to the pickling agent, the anodic reaction reducing Fe^{3+} to Fe^{2+}, for instance, takes place simultaneously with the above-mentioned reduction of H^+ so that the etching reaction of aluminum is encouraged to proceed. In order to depress the Fe^{2+} concentration which is increased with the progress of etching reaction, and to control the ferric ion concentration at a necessary level in the pickling agent, an oxidizing agent is concomitantly used.

[0004] However, there is the problem that since the oxidizing agent causes oxidative decomposition of a surfactant, the decomposition product of the surfactant accumulates in the pickling bath to sacrifice the degreasing action on the aluminum surface. There also is the problem that when the surfactant is added in excess to uphold the degreasing power, the running cost is inevitably increased.

[0005] Under the circumstances, many kinds of techniques have been developed for preventing decomposition of the surfactant with an oxidizing agent. The invention disclosed in Japanese Kokai Publication Hei-7-41973, for instance, comprises using a pickling agent containing an inorganic acid in a sufficient amount to establish a pH value not over pH 2, an oxidized metal ion, a surfactant, and a polyhydric alcohol having at least two hydroxyl groups directly attached to adjacent carbon atoms of its main chain in an amount of 0.1 to 5 g/l, with the intent of preventing decomposition of the surfactant with the polyhydric alcohol.

[0006] In the invention according to the above laid-open patent application, the pickling agent is supplementary added to the pickling bath using a first aqueous solution containing an inorganic acid and an oxidized metal ion and a second aqueous solution containing a surfactant, an oxidizing agent and a polyhydric alcohol with reference to the monitored redox potential of the pickling agent.

SUMMARY OF THE INVENTION

[0007] In order to uphold the degreasing power of the pickling bath agent, it is of paramount importance to control the surfactant concentration of the agent. However, when the surfactant is to be fed in the form of an aqueous solution containing an oxidizing agent as it is the case with the above prior art method, the variation in the surfactant concentration of the pickling bath becomes large because the addition amount of the oxidizing agent must be controlled according to the balance between the oxidized ion and the corresponding reduced ion.

[0008] Therefore, the present invention has for its object to provide a pickling kit such that it can be timely supplemented with a surfactant for upholding its degreasing power and be also timely supplemented with an oxidizing agent for reoxidizing the reduced ion for upholding its etching power and an associated pickling method.

[0009] The aluminum substrate pickling kit according to the present invention comprises a solution (A) containing sulfuric acid, a surfactant and an oxidized metal ion or anion and a solution (B) containing nitric acid and an oxidizing agent.

[0010] The oxidized metal ion mentioned above is preferably a ferric ion. As an example of the aluminum substrate to be cleaned, aluminum can bodies can be mentioned.

[0011] The pickling method for aluminum substrate according to the invention comprises supplementing, in the course of pickling of an aluminum substrate, a pickling agent with a solution (A) and a solution (B)

to thereby uphold the formulated components within the above concentration ranges,
said pickling agent containing 3000 to 50000 ppm of sulfuric acid, 100 to 5000 ppm of a surfactant, 50 to 3000 ppm of an oxidized metal ion or anion and 100 to 5000 ppm of nitric acid,
said solution (A) containing 30 to 500 mass parts of sulfuric acid, 1 to 50 mass parts of a surfactant, 0.5 to 30 mass parts of an oxidized metal ion or anion and 30 to 500 parts of water, and
said solution (B) containing 0.5 to 30 mass parts of nitric acid, 0.5 to 30 mass parts of an oxidizing agent and 10 to 300 mass parts of water.

[0012] In the above method of pickling an aluminum substrate, the timing of supplementation with said solution (A) is determined according to the electric conductivity of the pickling bath and that of said solution (B) is determined according to the redox potential of the pickling bath.

DETAILED DESCRIPTION OF THE INVENTION

[0013] The method of the present invention is now described in further detail.
[0014] In this description, the term "pickling kit" means the pickling agent which is used by separately adding the component solutions.
[0015] Of the pickling kit to be used for the pickling bath, the (A) solution contains sulfuric acid, a surfactant and an oxidized ion. The surfactant is used for the purpose of removing the oil adhering to the aluminum surface, for example the lubricating oil when the substrate to be cleaned is a DI-process aluminum can body. As the surfactant, any of nonionic, cationic, anionic and amphoteric surfactants can be employed. However, it is preferable to use a nonionic surfactant such as an alkyl alcohol-ethylene oxide adduct, an alkylphenol-ethylene oxide adduct, or an abietic acid derivative. The addition amount of the surfactant is preferably 1 to 50 mass parts, more preferably 5 to 30 mass parts, based on the total weight of the (A) solution. If the amount of the surfactant is less than 1 mass part, the degreasing power will be insufficient. If it exceeds 50 mass parts, the pickling bath will foam copiously to made cleaning difficult and increase the waste water treatment load.
[0016] The oxidized ion is used for oxidizing the aluminum substrate to aluminum ion (Al^{3+}) and thereby etching off the metal surface to facilitate formation of a chemical conversion film and improve adhesion of the film to the metal substrate. As examples of said oxidized ion, there can be mentioned oxidized metal ions such as ferric ion (Fe^{3+}), ceric ion (Ce^{4+}), cobaltic ion (Co^{5+}), stannic ion (Sn^{4+}), etc. and oxidized metal oxoanions such as metavanadate ion (VO^{3-}). These oxidized ions are preferably supplied in the form of water-soluble salts such as sulfates and nitrates . Thus, taking ferric ion as an example, ferric sulfate and ferric nitrate can be used with advantage. The addition amount of such oxidized ion in (A) solution is preferably 0.5 to 30 mass parts, more preferably 2 to 15 mass parts. When the addition amount is below 0.5 mass part, it is difficult to control the ion concentration in the pickling bath. Supplying the oxidized ion in excess of 30 mass parts tends to cause a precipitation problem due to excess supply.
[0017] The addition amount of sulfuric acid in (A) solution is preferably 30 to 500 mass parts, more preferably 100 to 300 mass parts. When the proportion of sulfuric acid is smaller than 30 mass parts, the necessary pH level of the pickling bath can hardly be established and upheld. When the limit of 500 mass parts is exceeded, the increased carryover of the acid to the next step will interfere with the chemical conversion reaction and cause an economic loss as well.
[0018] On the other hand, (B) solution contains nitric acid and an oxidizing agent. The oxidizing agent is used for reoxidizing the reduced ion formed on reduction of said oxidized metal ion by the oxidative etching of aluminum. For example, if the ferric ion only is supplementally added, the ferrous ion formed in the pickling agent accumulates in the pickling bath to encourage formation of a slurry and the precipitate derived from the ferrous ion adversely affects workability. Furthermore, since the cleaned aluminum product carries Fe ions over to the next step, a precipitate may form in the chemical conversion bath used in the next step so that the chemical conversion treatment is adversely affected. However, these disadvantages can be obviated by using an oxidizing agent.
[0019] The oxidizing agent which can be used in the present invention includes but is not limited to hydrogen peroxide (H_2O_2), persulfates (e.g. $NaS_2O_8{}^{2-}$), ozone (O_3), cerium compounds (e.g. ceric ammonium sulfate $(NH_4)_4Ce(SO_4)_2$) and nitrites (e.g. $NaNO_2$ and KNO_2). The amount of the oxidizing agent in (B) solution is preferably 0.5 to 30 mass parts, more preferably 2 to 15 mass parts. When the amount is below 0.5 mass part, it is difficult to uphold the oxidized ion at a necessary concentration in the pickling bath. On the other hand, supplying the oxidizing agent in excess of 30 mass parts causes decomposition of the surfactant so that the necessary surfactant concentration of the bath may not be upheld.
[0020] The amount of nitric acid in (B) solution is preferably 0.5 to 30 mass parts, more preferably 2 to 20 mass parts. When the amount is below 0.5 mass part, the aluminum substrate may not be uniformly etched. When it exceeds 30 mass parts, the waste water treatment load is increased and the economics of the process is sacrificed.
[0021] The pickling solution according to the present invention may contain various additives in addition to said

ingredients. For example, a polyhydric alcohol may be added to either (A) solution or (B) solution for preventing the decomposition of the surfactant by the oxidizing agent. This polyhydric alcohol has at least two hydroxyl groups directly attached to adjacent carbon atoms of its main chain, thus including dihydric alcohols such as 1,2-ethanediol (ethylene glycol), 1,2-propanediol (propylene glycol), 1,2-pentanediol, 1,2-butanediol, etc., trihydric alcohols such as 1,2,3-propanetriol (glycerol), 1,2,4-butanetriol, etc., and tetrahydric alcohols such as 1,2,3,4-butanetetraol etc., among others. The amount of said polyhydric alcohol in (A) solution or (B) solution is preferably 1 to 50 mass parts, more preferably 5 to 30 mass parts. Similarly for the purpose of preventing the surfactant decomposition by the oxidizing agent, a bromide ion may be added in a small proportion.

[0022] To clean the aluminum substrate with the pickling solution of the present invention, said (A) solution and nitric acid are appropriately blended to prepare a cleaning solution in the first place. This cleaning solution is prepared to a pH value of 0.6 to 2, a surfactant concentration of 100 to 5000 ppm, preferably 500 to 3000 ppm, and an oxidized ion concentration of 50 to 3000 ppm, preferably 200 to 1500 ppm.

[0023] The method of pickling an aluminum substrate according to the present invention can be carried into practice by whichever of the spraying technique and the dipping technique. In conducting this pickling, the treatment temperature is set to preferably 35 to 85 °C, more preferably 50 to 75 °C. When the treatment temperature exceeds 85 °C, overetching causes accelerated aging of the bath. When it is below 35 °C, insufficient etching and, hence, poor desmutting are inevitable. The pickling time is preferably 30 to 300 seconds. If the duration of treatment exceeds 300 seconds, overetching will cause accelerated aging of the bath. If it is less than 30 seconds, insufficient etching will result in poor desmutting. More preferred pickling time is 45 to 120 seconds.

[0024] The amount of supplemental addition of (A) solution is preferably selected according to the measured electrical conductivity of the pickling bath. Since the electrical conductivity depends on the electrolyte concentration of the bath, the conductivity value drops as the sulfuric acid is carried off with the aluminum substrate and the aluminum ion is eluted out of the aluminum substrate. Preferred electrical conductivity value is 10 to 100 mS/cm, preferably 30 to 70 mS/cm. By supplemental addition of (A) solution, the surfactant concentration can be upheld within the above-mentioned conductivity range.

[0025] The amount of supplemental addition of (B) solution is preferably selected according to the measured redox potential of the pickling bath. Since the redox potential depends on the ratio of oxidized ion to reduced ion in the bath, it drops as the oxidized ion is consumed by reduction. Taking ferric oxide as an example, the preferred redox potential is 0.4 to 0.7 mV (vs. Ag/AgCl), more preferably 0.5 to 0.6 mV. When this redox potential is less than 0.4 mV, the oxidized ion is deficient so that the amount of etching of the aluminum surface tends'to be decreased. On the other hand, when it exceeds 0.7 mV, the oxidizing agent is excessively supplied to accelerate decomposition of the surfactant and, moreover, an economic loss results.

[0026] As the oxidizing agent is added by supplemental addition of (B) solution, the reduced ion is oxidized to uphold the etching power. By this method, even if a variation takes place in the number of aluminum can bodies to be pickled, the amount of the (B) solution to be supplementary added can be mechanically determined according to the change in redox potential. Moreover, since the oxidizing agent and surfactant are not supplied in one and the same solution unlike in the prior art, it does not happen that a change in amount of the oxidizing agent affects the surfactant concentration to cause poor degreasing and associated black discoloration of the aluminum can bottom in the sterilization step.

[0027] The aluminum surface cleaned with the pickling kit of the present invention can be rinsed with water and subjected to a chemical conversion treatment using, for example, a chromating agent such as chromic acid-chromate, phosphate-chromate and the like system or a chromium-free treating agent such as zirconium phosphate, titanium phosphate and the like, in the routine manner.

[0028] In the pickling kit of the invention, a solution (A) contains sulfuric acid, a surfactant and an oxidized metal ion or anion while a solution (B) contains nitric acid and an oxidizing agent. Therefore, it does not course the decrease in degreasing power and the associated black discoloration due to the effect of the variation of the amount the oxidizing agent on the surfactant concentration.

[0029] Moreover, when the timing of supplementation with said solution (A) is determined according to the electric conductivity of the pickling bath, the surfactant concentration can be stabilized, while, when the timing of supplementation with said solution (B) is determined according to the redox potential of the pickling bath, the oxidizing agent concentration can be stabilized.

EXAMPLE

(1) Substrate

[0030] Lid-free can bodies carrying lubricating oil and smut'as obtained by DI processing of the 3004 aluminum alloy plate were used.

(2) Pickling agent (initial bath composition)

[0031] A pickling agent was prepared according to the recipe; sulfuric acid: 20000 ppm, a surfactant: 2000 ppm, Fe^{3+}: 500 ppm and nitric acid: 1000 ppm, and used as a treating bath.

(3) Pickling solutions (supplemental agents)

[0032] A solution (A) containing 200 mass parts of sulfuric acid, 20 mass parts of a surfactant, 5 mass parts of Fe^{3+} and 300 mass parts of water and a solution (B) containing 10 mass parts of nitric acid, 10 mass parts of hydrogen peroxide and 150 mass parts of water were prepared for use as supplemental agents.

(4) Treating conditions

[0033] The electric conductivity and redox potential of the pickling bath were measured, and the solution (A) was added when the electric conductivity value had reached 35 mS/cm or less while the solution (B) was added when the redox potential had dropped to 520 mV or less. The can bodies were treated continuously at the rate of 48000 cans/hr, 72000 cans/hr, or 96000 cans/hr for 24 consecutive hours. The temperature of the pickling bath was 75 °C and the pickling time was 50 seconds (spray treatment) . After pickling, the can bodies were rinsed with tap water for 15 seconds and, then, subjected to chemical conversion treatment with a conversion reagent ("Alsurf 440", Nippon Paint) at 40 °C for 12 seconds. The treated can bodies were rinsed with tap water for 15 seconds, spray-washed with deionized water for 5 seconds, and dried at 190 °C for 3 minutes .

(5) Evaluation

[0034] The pickling bath composition after 24 hours of treatment was analyzed by Cesibor titrimetry for the surfactant, redox titrimetry for Fe^{3+}, and TOC (total organic carbon) -metry ("TOC 5000", Shimadzu Corporation) for oil. In addition, from among the cans treated just before the end of the treatment session, 10 cans were randomly taken out and the bottoms were cut out and immersed in tap water at 100 °C for 30 minutes to evaluate boiling water resistance. The results are shown in Table 1.

Comparative Example

[0035] As supplemental agents, a solution (A) containing 200 mass parts of sulfuric acid, 10 mass parts of nitric acid, 5 mass parts of Fe^{3+} and 300 mass parts of water and a solution (B) containing 20 mass parts of surfactant, 10 mass parts of hydrogen peroxide and 150 mass parts of water were respectively prepared. Otherwise, the procedure of Example 1 was faithfully followed to treat can bodies, and the surfactant concentration, oil (grease) concentration and boiling water resistance were measured and evaluated. The results are shown in Table 1.

Table 1

	Treatment load (cans/hr)	Concentrations of agent components after treatment of can bodies			Evaluation of cans (boiling water resistance)
		Surfactant	Oil	Fe^{3+}	
Example	48000	1800 ppm	700 ppm	350 ppm	Not tarnished
	72000	1900 ppm	1000 ppm	360 ppm	Not tarnished
	96000	1900 ppm	1200 ppm	350 ppm	Not tarnished
Compar. Example	48000	800 ppm	700 ppm	360 ppm	Overall punctate blacking
	72000	1300 ppm	1000 ppm	350 ppm	Local punctate blacking
	96000	1800 ppm	1300 ppm	360 ppm	Not tarnished

[0036] It will be apparent from the above results that by adjusting the bath composition with the supplemental agents according to the Examples, both the surfactant concentration and Fe^{3+} concentration can be judiciously controlled so that can bodies can be sufficiently pickled to enable formation of a wholesome chemical conversion film. Therefore, the boiling water resistance of can bodies is also excellent. Incidentally, the treatment of 96000 cans in Comparative Example appears satisfactory at a first glance but in a commercial production line, the treatment load varies in the order of tends of thousand cans at the maximum. It can be seen that, in Examples, a stable treatment is feasible even when such changes occur in the treatment load.

Claims

1. A pickling kit for an aluminum substrate
which comprises a solution (A) containing sulfuric acid, a surfactant and an oxidized metal ion or anion and a solution (B) containing nitric acid and an oxidizing agent.

2. The pickling kit for an aluminum substrate according to Claim 1
wherein said oxidized metal ion is ferric ion.

3. The pickling kit for an aluminum substrate according to Claim 1 or 2
wherein said aluminum substrate is an aluminum can body.

4. The pickling method for aluminum substrate

which comprises supplementing, in the course of pickling of an aluminum substrate, a pickling agent with a solution (A) and a solution (B)
to thereby uphold the formulated components within the above concentration ranges,
said pickling agent containing 3000 to 50000 ppm of sulfuric acid, 100 to 5000 ppm of a surfactant, 50 to 3000 ppm of an oxidized metal ion or anion and 100 to 5000 ppm of nitric acid,
said solution (A) containing 30 to 500 mass parts of sulfuric acid, 1 to 50 mass parts of a surfactant, 0.5 to 30 mass parts of an oxidized metal ion or anion and 30 to 500 parts of water, and
said solution (B) containing 0.5 to 30 mass parts of nitric acid, 0.5 to 30 mass parts of an oxidizing agent and 10 to 300 mass parts of water.

5. The method of pickling an aluminum substrate according to Claim 4
wherein the timing of supplementation with said solution (A) is determined according to the electric conductivity of the pickling bath and the timing of supplementation with said solution (B) is determined according to the redox potential of the pickling bath.