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(54) **AQUEOUS ACID CLEANING SOLUTION FOR ALUMINUM METAL AND METHOD FOR
CLEANING THE METAL**

(57) An aqueous acid cleaning solution for aluminum metals which contains oxidized metal ions as an etching accelerator and does not contain hazardous fluorine and chromium ions. The solution contains an inorganic acid, oxidized metal ions, a chelate dispersant, if necessary a surfactant, and further an oxidizing agent for the metal ions reduced by cleaning. The dispersant has the effect of inhibiting the formation of a sludge from the oxidized metal, thus permitting the preparation of a sludge-free aqueous acid cleaning solution.

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Description

Technical Field

5 The present invention relates to an acidic cleaning aqueous solution for an aluminum based metal and a process for cleaning the same, and more particularly, it relates to a cleaning aqueous solution which can satisfactorily remove a lubricant, an aluminum powder or the like attached on an aluminum surface at the time of molding, and a method cleaning the aluminum surface.

10 Background Art

A product having an aluminum surface, for example, an aluminum container for a drink made of an aluminum-based metal, i.e., aluminum or an aluminum alloy, can usually be manufactured by a molding operation called drawing and ironing (hereinafter referred to as "DI"). In this molding operation, a lubricant is applied onto a metal surface, and particularly on the inside wall of the obtained container, an aluminum powder (a smut) is deposited. The surface of this kind of container is usually protected by a subsequent chemical-conversion treatment or paint coating. Therefore, it is necessary that the above-mentioned lubricant or smut should be removed from the metal surface prior to this chemical-conversion treatment or the like to clean the metal surface.

For the sake of this surface cleaning, there has usually been used an acidic cleaning agent for suitably etching the metal surface to clean it. Heretofore, as such an acidic cleaning agent, chromium-based and hydrofluoric acid-based cleaning agents have often been used. In particular, the hydrofluoric acid-based cleaning agents are excellent in that low-temperature cleaning (50°C or less) is possible. However, the above-mentioned cleaning agents are harmful substances, and therefore waste water controls are strict. Hence, in recent years, it has been desired to establish a chromium-free and fluorine-free low-temperature acidic cleaning technique.

25 Such chromium-free and fluorine-free acidic cleaning techniques have been suggested in Japanese Patent Publication No. 50838/1991 entitled "Aluminum Surface Cleaning agent" and Japanese Patent Publication No. 65436/1991 entitled "Control Method of Aluminum Surface Cleaning agent".

In Japanese Patent Publication No. 50838/1991 entitled "Aluminum Surface Cleaning agent" and Japanese Patent Publication No. 65436/1991 entitled "Control Method of Aluminum Surface Cleaning agent", there have been disclosed an acidic cleaning agent in which very little or no fluorine ions are contained and a pH is adjusted to 2 or less with sulfuric acid and/or nitric acid, and ferric ions for promoting etching are further contained in place of the fluorine ions, and a control method which comprises controlling an oxidation-reduction potential of a cleaning bath to control the concentration of the ferric ions in the bath.

Usually, the etching reaction of aluminum in the acidic cleaning agent comprises an anodic reaction in which aluminum becomes aluminum ions (Al^{3+}), and a cathodic reaction in which H^+ in the cleaning agent is reduced to $1/2 \text{H}_2$. Thus, when the acidic cleaning agent containing the ferric ions (Fe^{3+}) is added, the anodic reaction in which this Fe^{3+} is reduced to Fe^{2+} occurs simultaneously with the above-mentioned reduction of H^+ , so that the etching reaction of aluminum is promoted.

In addition, when the oxidation-reduction potential of the cleaning agent bath is controlled by the use of an oxidizing agent to control the concentration of the ferric ions in the bath, the concentration of Fe^{2+} which increases with the progress of the aluminum etching reaction can be inhibited and Fe^{2+} can be oxidized to Fe^{3+} .

However, in the acidic cleaning agents disclosed in Japanese Patent Publication No. 50838/1991 and Japanese Patent Publication No. 65436/1991, the iron ions are contained, and therefore, in the case that the acidic aqueous solution is diluted, a precipitate (a sludge) is derived from the iron ions, particularly, hydroxides are generated. In addition, there is a problem that, in a precleaning step which is a step before main cleaning, the sludge is stuck on a heater portion of a tank.

Disclosure of the Invention

50 The present invention has been developed with the intention of solving such problems. Thus, an object of the present invention is to provide an acidic cleaning aqueous solution for an aluminum-based metal which contains oxidizing metal ions as an etching promotor but contains neither harmful fluorine nor chromium ions and which can carry out acidic cleaning, and another object of the present invention is to provide a method for cleaning the aluminum-based metal.

55 In order to achieve these objects, the acidic cleaning aqueous solution for an aluminum-based metal regarding the present invention is characterized by containing an inorganic acid in an amount necessary to become pH 2 or less, oxidizing metal ions and a chelating dispersant.

Furthermore, the acidic cleaning aqueous solution for an aluminum-based metal regarding the present invention is characterized by containing an inorganic acid in an amount necessary to become pH 2 or less, oxidizing metal ions, a

surfactant and a chelating dispersant.

In addition, according to the present invention, there is provided a method for cleaning an aluminum surface which comprises the steps of preparing an acidic cleaning aqueous solution containing at least one selected from inorganic acids in an amount necessary to become pH 2 or less, oxidizing metal ions, a chelating dispersant and a surfactant which may be used in compliance with degreasing requirement, feeding "the oxidizing metal ions and an oxidizing agent" or "the oxidizing agent" to the acidic cleaning aqueous solution, and then measuring an oxidation-reduction potential of the aqueous solution to maintain and control the concentration of the oxidizing metal ions in the aqueous solution.

The above-mentioned acidic cleaning aqueous solution can be used as a cleaning bath for cleaning a material of the aluminum-based metal, but this cleaning bath can be obtained by diluting a concentrated aqueous solution of the above-mentioned acidic cleaning aqueous solution with a suitable amount of water to a concentration in a usable concentration range.

In the first place, examples of the inorganic acid include sulfuric acid and nitric acid will be given.

Examples of the oxidizing metal ions include ferric ions (Fe^{3+}), metavanadic ions (VO_3^-), cerium(IV) ions (Ce^{4+}), cobalt ions (Co^{5+}) and tin ions (Sn^{4+}). Above all, the ferric ions (Fe^{3+}) and the metavanadic ions (VO_3^-) are preferable. In this connection, the oxidizing metal ions means metal ions having a higher valence in the case that the metal has a plurality of valences.

Examples of the feed source of the ferric ions include water-soluble ferric salts such as ferric sulfate, ferric nitrate and ferric perchlorate. Examples of the feed source of the metavanadic ions include sodium metavanadate, potassium metavanadate and ammonium metavanadate. An example of the feed source of the cerium(IV) ions is ammonium cerium (IV) sulfate. Examples of the feed source of the cobalt ions include cobalt(V) sulfate and ammonium cobalt(V) sulfate. Examples of the feed source of the tin ions include stannic sulfate and stannic nitrate.

As the chelating dispersant which can be used in the present invention, any compound can be used, so long as it can form a chelate with the oxidizing metal ions, can stabilize the oxidizing metal ions in the aqueous solution under a strong acid, and can improve dispersibility in the aqueous solution under the strong acid. Preferably, a phosphonic acid compound is used. Examples of the preferably usable phosphonic acid compound include 1-hydroxyethylidene-1,1-diphosphonic acid, aminotri(methylenephosphonic acid) and ethylenediaminetetra(methylenephosphonic acid).

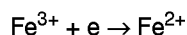
As the surfactant, there can be used conventional surfactants of all kinds of nonionic, cationic, anionic and amphoteric systems. Above all, particularly preferable are nonionic surfactants such as ethoxylated alkylphenols, hydrocarbon derivatives, abietic acid derivatives, ethoxylated primary alcohols and modified polyethoxylated alcohols.

In addition, it is preferable to add bromine ion and/or polyhydric alcohol as a decomposition inhibitor for the surfactant.

Examples of the feed source of the bromide ion include a 47% aqueous HBr solution, potassium bromide, sodium bromide, aluminum bromide and iron bromide.

As the polyhydric alcohol, an alcohol having, in one molecule, at least two hydroxyl groups directly bonded to an adjacent carbon atom in a main chain is preferable, and examples of the polyhydric alcohol include divalent alcohols such as 1,2-ethanediol (ethylene glycol), 1,2-propanediol (propylene glycol), 1,2-pentanediol and 1,2-butanediol, trivalent alcohols such as 1,2,3-propanetriol (glycerin) and 1,2,4-butanetriol, and a tetravalent alcohol such as 1,2,3,4-butanetetraol.

In general, when cleaning is carried out and in the case that the ferric ions are used as the oxidizing metal ions, the ferric ions change into ferrous ions in accordance with



with the lapse of time, so that an oxidation-reduction potential lowers (which is also called the aging of the cleaning bath), with the result that an etching promotion effect on the aluminum surface is lost. Similarly with regard to the metavanadic ions, the aging of the cleaning bath proceeds with time. Thus, in the case that the ferric ions are used as the oxidizing metal ions, the ferric ions can be fed on occasion, or an ORP control oxidizing agent may be added on occasion to oxidize the ferrous ions to the ferric ions. Here, examples of the ORP control oxidizing agent include hydrogen peroxide (H_2O_2), persulfates (e.g., $\text{Na}_2\text{S}_2\text{O}_8^{2-}$), ozone (O_3), cerium compounds [e.g., ammonium cerium (IV) sulfate: $(\text{NH}_4)_4\text{Ce}(\text{SO}_4)_4$], nitrites (e.g., NaNO_2 and KNO_2) and compounds capable of producing the metavanadic ions (VO_3^-). Incidentally, these oxidizing agents are disclosed in Japanese Patent Publication No. 65436/1991. In this connection, the means an oxidation-reduction potential.

Furthermore, the acidic cleaning aqueous solution of the present invention is preferably adjusted to pH 2 or less, more preferably pH 0.6 to 2 with an inorganic acid. If the pH is more than 2, the etching velocity on the aluminum surface deteriorates extremely, so that the effectiveness of the cleaning bath is scarcely exerted. On the other hand, if the pH is less than 0.6, economy is poor, and the amount of the aqueous solution carried to a chemical step of a next step increases, which causes a chemical-conversion failure.

The oxidizing metal ions are preferably contained in an amount of 0.05 to 4 g/l, more preferably 0.2 to 2 g/l in the

acidic cleaning aqueous solution. If the content of the oxidizing metal ions is less than 0.05 g/l, the amount of the etched metal is insufficient, so that the removal of the smut tends to be insufficient. On the other hand, even if it is more than 4 g/l, no additional cleaning effect can be observed, which is uneconomical.

5 The chelating dispersant is preferably contained in an amount of 0.05 to 5 g/l, more preferably 0.1 to 2 g/l in the acidic cleaning aqueous solution. If the content of the chelating dispersant is less than 0.05 g/l, the chelating is not sufficient, so that hydroxides of the oxidizing metal are formed, with the result that a precipitate (a sludge) is generated in the aqueous solution. In addition, on a heater portion in the precleaning step, the hydroxides of the oxidizing metal are sometimes accumulated. In the case that the cleaning method of the present invention is carried out by a spray, a spray riser and a spray nozzle are liable to be clogged. Even if it is more than 5 g/l, no additional chelating dispersion effect
10 can be observed, which is uneconomical.

The surfactant is preferably contained in an amount of 0.1 to 10 g/l, more preferably 0.5 to 2 g/l in the acidic cleaning aqueous solution. If the content of the surfactant is less than 0.1 g/l, cleaning properties, particularly degreasing properties, tend to deteriorate. On the other hand, even if it is more than 10 g/l, no additional cleaning effect can be observed, which is uneconomical.

15 The bromide ion is preferably contained in an amount of 0.002 to 0.1 g/l in the acidic cleaning aqueous solution. If the content of the bromide ion is less than 0.002 g/l, the inhibition effect of the oxidative decomposition reaction of the surfactant tends to deteriorate, and even if it is more than 0.1 g/l, no additional inhibition effect of the oxidative decomposition reaction of the surfactant can be obtained.

20 The polyhydric alcohol having, in one molecule, at least two hydroxyl groups directly bonded to an adjacent carbon atom in a main chain is preferably contained in an amount of 0.1 to 5 g/l, more preferably 0.2 to 3 g/l in the acidic cleaning aqueous solution. If the content of the polyhydric alcohol having the above-mentioned structure is less than 0.1 g/l, the inhibition effect of the decomposition reaction tends to be insufficient. On the other hand, if it is more than 5 g/l, no additional cleaning effect can be obtained, which is uneconomical. In addition, since the concentration of the polyhydric alcohol is high, the load of a waste water treatment increases inconveniently.

25 The acidic cleaning bath is preferably controlled to an oxidation-reduction potential (an ORP) of 0.5 to 0.8 V (vs. Ag/AgCl). If the acidic cleaning bath is less than 0.5 V, the oxidizing metal ion is insufficient, so that the amount of an etched aluminum surface is liable to be insufficient. On the other hand, if it is more than 0.8 V, economy is poor. The preferable oxidation-reduction potential is in the range of 0.55 to 0.7 (vs. Ag/AgCl).

In the case that the ferric ions are used as the oxidizing metal ions in the acidic cleaning bath, the ferrous ions (Fe²⁺) are accumulated in the acidic cleaning bath, if the ferric ions (Fe³⁺) alone are fed. As a result, the acidic cleaning bath becomes a sludge state, and a precipitate derived from the ferrous ions is formed and a treatment operativity deteriorates. In addition, an article to be treated such as an aluminum can carried from the acidic cleaning bath brings the iron ions to the next step, and in consequence, a precipitate might be generated in the next step and the chemical-conversion treatment might be inversely affected. Therefore, "the oxidizing metal ions and the oxidizing agent" or "the oxidizing agent" should be fed to the acidic cleaning bath to maintain and control the oxidation-reduction potential (the ORP) in the above-mentioned range, whereby the above-mentioned problems can be solved.
30

35 In the acidic cleaning method of the aluminum surface according to the present invention, either of a spray method and an immersion method may be used. In carrying out the acidic cleaning, a treatment temperature is preferably in the range of 35 to 80°C, more preferably 50 to 70°C. If the treatment temperature is more than 80°C, the etching is excessive, so that the aging of the cleaning bath is accelerated. On the other hand, if it is less than 35°C, the amount of the etched aluminum surface is insufficient, so that the removal of the smut tends to be insufficient.
40

A acidic cleaning time is preferably in the range of 30 to 300 seconds. If the treatment time is more than 300 seconds, the etching is excessive, so that the aging of the cleaning bath is accelerated. On the other hand, if it is less than 30 seconds, the amount of the etched aluminum surface is insufficient, so that the removal of the smut tends to be insufficient. A more preferable treatment time is in the range of 45 to 120 seconds.
45

The aluminum surface which has been cleaned by the acidic cleaning agent of the present invention may be washed with water and then subjected to a phosphate chemical-conversion treatment in a normal manner.

50 According to the present invention, the chelating dispersant can particularly be used, whereby a chelate can be formed in the acidic aqueous solution with the aid of the oxidizing metal ion and a chelate dispersant, and the dispersibility of the oxidizing metal ion in the acidic aqueous solution can be improved, whereby the generation of a precipitate (a sludge) of hydroxides of the oxidizing metal ion can be prevented. In consequence, the satisfactory cleaning of the aluminum-based metal surface can be achieved without any generation of the sludge.

Best Mode for Carrying out the Invention

55 Next, the present invention will be described in detail with reference to examples and comparative examples.

Examples 1 to 16 and Comparative Examples 1 to 4

(1) Articles to be treated:

5 Containers without a lid which were obtained by subjecting an aluminum plate of a 3004 alloy to a DI process and on which a lubricant and a smut were deposited.

(2) Cleaning agents:

10 Acidic cleaning aqueous solutions were used which were constituted of addition amounts described in items of Example and Comparative Examples shown in Table 1 given below.

(3) Treatment conditions:

15 The above-mentioned containers were spray-treated at 70 to 75°C for 60 seconds with the respective cleaning agents, next spray-washed with tap water for 15 seconds and successively with deionized water for 5 seconds, and then dried at 95°C.

(4) Evaluation of cleanability:

20 The following items were tested. The results are shown in Tables 1 and 2.

(a) Appearance:

25 A whiteness of each dried container was visually judged. A sample having a white appearance, in which degreasing and desmutting are perfect and etching is sufficiently made, is estimated to be good, and the evaluation is ranked on the basis of the following five steps in accordance with the degree of the whiteness.

30 ◎: Wholly white
○: Partially light gray
△: Wholly light gray
x: Partially gray
xx: Wholly gray

35 (b) Water wetness:

Immediately after the spray-washing with water, each container is shaken three times to drain water, and the container is allowed to stand upright. After 30 seconds, a water wet area (%) on the outside surface of the container is measured.

40 (c) Desmutting properties:

A transparent adhesive tape is stuck on the inside surface of the dried container, and this tape is peeled therefrom and then stuck on a white mount. Next, a whiteness of the stuck tape is compared with that of the other white mount portion. The dirt-free sample in which the smut has been completely removed is estimated to be good, and the evaluation is ranked on the basis of the following five steps in accordance with the degree of the dirt.

5: No dirt
50 4: traces of dirt
3: Slight dirt
2: Appreciable dirt
55 1: Serious dirt

(5) Sludge preventing properties:

The cleaning agent used in the evaluation of the cleaning properties is diluted 20 times with water, and then heated (60°C for 1 day) by an electric heater. Afterwards, a stuck sludge state on the electric heater is evaluated on the basis of the following three steps.

- 3: A case where no sludge is stuck
- 2: A case where sludge is slightly stuck
- 1: A case where sludge is wholly stuck

The results of the evaluation will be shown in the following. Furthermore, the basic components of an acidic cleaning bath were fed from 75% sulfuric acid and 67.5% nitric acid, and ferric ions (Fe^{3+}) were fed from 41% ferric sulfate $[\text{Fe}_2(\text{SO}_4)_3]$, and Ce^{4+} was fed from cerium(IV) sulfate $[\text{Ce}(\text{SO}_4)_2]$.

Table 1

Inorganic Acid			Oxidizing Metal Ions		Chelating Disper- sant		Nonionic Surfactant			pH	
	H ₂ SO ₄ (g/l)	HNO ₃ (g/l)	Fe ³⁺ (g/l)	Ce ⁴⁺ (g/l)	Kind (g/l)		Kind (g/l)				
Example											
1	12.5	-	1.0	-	A	1.0	-	-	-	-	0.9
2	12.5	-	1.0	-	B	1.0	-	-	-	-	0.9
3	12.5	-	1.0	-	A	1.0	(1) ^{1*}	1.0	(2) ^{*2}	1.0	0.9
4	12.5	-	1.0	-	B	1.0	(1)	1.0	(2)	1.0	0.9
5	12.5	-	1.0	-	C	1.0	(1)	1.0	(2)	1.0	0.9
6	-	12.5	1.0	-	A	1.0	(1)	1.0	(2)	1.0	0.9
7	10.0	2.5	1.0	-	A	1.0	(1)	1.0	(2)	1.0	0.9
8	12.5	-	0.2	-	A	1.0	(1)	1.0	(2)	1.0	0.9
9	12.5	-	0.2	-	A	0.1	(1)	1.0	(2)	1.0	0.9
10	12.5	-	1.0	-	A	1.0	(3) ^{*3}	1.0	(2)	1.0	0.9
11	5.0	-	1.0	-	A	1.0	(1)	1.0	(2)	1.0	1.8
12	12.5	-	1.0	-	A	1.0	(1)	0.25	(2)	0.25	0.9
13	12.5	-	4.0	-	A	5.0	(1)	1.0	(2)	1.0	0.9
14	12.5	-	1.0	-	A	0.5	(1)	1.0	(2)	1.0	0.9
		-			B	0.5					
15	12.5	-	0.05	-	A	0.05	(1)	1.0	(2)	1.0	0.9
16	10.0	2.5	-	1.0	A	1.0	(1)	1.0	(2)	1.0	0.9
COMPARA- TIVE EXAM- PLE											
1	12.5	-	1.0	-	-	-	-	-	-	-	0.9
2	12.5	-	1.0	-	-	-	(1)	1.0	(2)	1.0	0.9
3	12.5	-	0.2	-	-	-	(1)	1.0	(2)	1.0	0.9
4	3.0	-	1.0	-	-	-	(1)	1.0	(2)	1.0	2.5

Notes:

*1: Nonylphenolic EO adduct (1),

*2: Hydrocarbon derivative (2),

*3: Abietic acid derivative (3),

*4:

A ... 1-hydroxyethylidene-1,1-diphosphonic acid,

B ... Aminotri(methylenephosphonic acid), and

C ... Ethylenediaminetetra(methylenephosphonic acid)

In Example 14 in Table 1, two kinds of chelating dispersants were used.

Table 2

	Result of Evaluation			
	Sludge Preventing Properties (%)	Cleaning Properties		
		Appearance	Water Wetness(%)	Desmutting Properties
<u>Example</u>				
1	3	○	80	4
2	3	○	80	4
3	3	⊙	100	5
4	3	⊙	100	5
5	3	⊙	100	5
6	3	⊙	100	5
7	3	⊙	100	5
8	3	○	100	4
9	3	○	100	4
10	3	⊙	100	5
11	3	○	100	5
12	3	⊙	100	5
13	3	⊙	100	5
14	3	⊙	100	5
15	3	○	100	4
16	3	⊙	100	5
<u>Comparative Example</u>				
1	1	△	0	1
2	1	⊙	100	5
3	2	○	100	4
4	1	△	80	3

Example 17

The same procedure as in Example 3 was repeated except that 0.04 g/l of bromide ion was added to the cleaning agent of Example 3. The results were the same as in Example 3, and all the evaluation items were good.

From these results, it is apparent that good cleaning can be obtained, without using any fluorine ions, by the use of the acidic cleaner and a cleaning bath for an aluminum-based metal according to the present invention.

Example 18 (Performance change by ORP value)

Table 3

1-Hydroxyethylidene-1, 1-diphosphonic acid	1.0g/l
H ₂ SO ₄	12.5g/l
Fe ²⁺	1.0g/l
Nonylphenolic EO adduct	1.0g/l
Hydrocarbon derivative	1.0g/l

H₂O₂ was added in different amounts to the above-mentioned aqueous solution (solution temperature = 70°C), and performances at ORPs of 0.60, 0.50 and 0.45 V (vs. Ag/AgCl) were then evaluated.

Table 4

ORP(vs. Ag/AgCl)	Appearance	Water Wetness(%)	Desmutting Properties
0.60V	⊙	100	5
0.50V	○	100	4
0.45V	△	100	3

Examples 19 to 24

(1) Articles to be treated:

Containers without a lid which were obtained by subjecting an aluminum plate of a 3004 alloy to a DI process and on which a lubricant and a smut were deposited.

(2) Cleaning agents:

An acidic cleaning aqueous solution was employed which was used in the undermentioned "(4) Oxidizing efficiency evaluation" and in which ferrous ions in the cleaning aqueous solution were oxidized to ferric ions by hydrogen peroxide.

(3) Treatment conditions:

The above-mentioned containers were spray-treated at 70°C for 60 seconds with the respective cleaning agents, next spray-washed with tap water for 15 seconds and successively with deionized water for 5 seconds, and then dried at 95°C.

(4) Evaluation of oxidizing efficiency:

Hydrogen peroxide was added dropwise while the acidic cleaning aqueous solution constituted of addition amounts described in examples shown in Table 5 given below was heated at 70°C and stirred. An oxidizing efficiency was calculated in accordance with the following equation.

$$\text{Oxidizing efficiency} = (a/b) \times 100 (\%)$$

wherein a is an amount of hydrogen peroxide theoretically required in oxidizing the ferrous ions (Fe²⁺) to ferric ions (Fe³⁺), and b is an amount of actually required hydrogen peroxide.

Evaluation was made on the basis of the following two steps.

- ⊙: 80-100 (%)
○: 60-80 (%)

(5) Evaluation of cleanability:

The following items were tested. The results are shown in Table 6. Furthermore, with regard to appearance, water wetness and desmutting properties, the evaluation standards used for the evaluation of Examples 1 to 16 and Comparative Examples 1 to 4 were applicable.

Table 5

	Inorganic Acid	Oxidizing Metal Ions	Chelating ^{*3} Dispersant	Nonionic Surfactant		Additive for inhibition of oxidative decomposition reaction	pH
	H ₂ SO ₄ (g/l)	Fe ³⁺ (g/l)	Kind (g/l)	Kind (g/l)	Kind (g/l)	Kind (g/l)	
<u>Example</u>							
19	12.5	1.0	A	(1) ^{1*}	(2) ^{*2}	Bromide ions	0.9
			1.0	1.0	1.0	0.02	
20	12.5	1.0	A	(1)	(2)	Bromide ions	0.9
			1.0	1.0	1.0	0.2	
21	12.5	1.0	A	(1)	(2)	Ethylene glycol	0.9
			1.0	1.0	1.0	0.5	
22	12.5	1.0	A	(1)	(2)	Ethylene glycol	0.9
			1.0	1.0	1.0	3.0	
23	12.5	1.0	A	(1)	(2)	Glycerin	0.9
			1.0	1.0	1.0	0.5	
24	12.5	1.0	A	(1)	(2)	Glycerin	0.9
			1.0	1.0	1.0	3.0	

Notes:

*1: Nonylphenolic EO adduct (1),

*2: Hydrocarbon derivative (2),

*3: A ... 1-hydroxyethylidene-1,1-diphosphonic acid, table 6

Table 6

	Result of Evaluation			
	Judgement of Oxidation Efficiency (%)	Cleaning Properties		
		Appearance	Water Wetness(%)	Desmutting Properties
<u>Example</u>				
19	○	◎	100	5
20	◎	◎	100	5
21	○	◎	100	5
22	◎	◎	100	5
23	○	◎	100	5
24	◎	◎	100	5

Example

As described above, according to an acidic cleaning agent, a cleaning bath and a cleaning method for an aluminum-based metal regarding the present invention, a lubricant and a smut stuck on the aluminum surface can be removed therefrom without using harmful chromium ions and fluoride ions which bring about environmental pollution and pollute an operational environment. In addition, cleaning can be carried out so that a chemical-conversion treatment and a coating operation can be carried out in order.

Possibility of Industrial Utilization

The present invention can be applied to a cleaning aqueous solution and a cleaning method for removing a lubricant and an aluminum powder (a smut) stuck on a metal surface, in manufacturing an aluminum container for a drink made of an aluminum-based metal, i.e., aluminum or an aluminum alloy by a molding operation called drawing and ironing (hereinafter referred to as "DI").

Claims

1. An acidic cleaning aqueous solution for an aluminum-based metal which comprises:

an inorganic acid in an amount necessary to become pH 2 or less;
oxidizing metal ions; and
a chelating dispersant.

2. An acidic cleaning aqueous solution for an aluminum-based metal which comprises:

an inorganic acid in an amount necessary to become pH 2 or less;
oxidizing metal ions;
a chelating dispersant; and
a surfactant.

3. The acidic cleaning aqueous solution for an aluminum-based metal according to Claim 1 or 2, wherein the oxidizing metal ions are ferric ions, metavanadic ions or cerium(IV) ions.

4. The acidic cleaning aqueous solution for an aluminum-based metal according to Claim 1 or 2, wherein the oxidizing metal ions are contained in an amount of 0.05 to 4 g/l in the acidic aqueous solution.

5. The acidic cleaning aqueous solution for an aluminum-based metal according to Claim 1 or 2, wherein the inorganic acid is sulfuric acid or nitric acid.

6. The acidic cleaning aqueous solution for an aluminum-based metal according to Claim 1 or 2, wherein a pH of the acidic cleaning aqueous solution is in the range of 0.6 to 2.

7. The acidic cleaning aqueous solution for an aluminum-based metal according to Claim 1 or 2, wherein the chelating dispersant is a phosphonic acid compound.

8. The acidic cleaning aqueous solution for an aluminum-based metal according to Claim 1 or 2, wherein the chelating dispersant is at least one phosphonic acid compound selected from the group consisting of 1-hydroxyethylidene-1,1-diphosphonic acid, aminotri(methylenephosphonic acid) and ethylenediaminetetra(methylenephosphonic acid).

9. The acidic cleaning aqueous solution for an aluminum-based metal according to Claim 1 or 2, wherein the chelating dispersant is contained in an amount of 0.05 to 5 g/l in the acidic aqueous solution.

10. The acidic cleaning aqueous solution for an aluminum-based metal according to Claim 1 or 2, wherein the surfactant is at least one nonionic surfactant selected from the group consisting of ethoxylated alkylphenols, hydrocarbon derivatives and abietic acid derivatives.

11. The acidic cleaning aqueous solution for an aluminum-based metal according to Claim 1 or 2, wherein the surfactant is contained in an amount of 0.1 to 10 g/l in the acidic aqueous solution.

12. The acidic cleaning aqueous solution for an aluminum-based metal according to Claim 1 or 2, further having a bromide ions and/or a polyhydric alcohol added.
- 5 13. The acidic cleaning aqueous solution for an aluminum-based metal according to Claim 12, wherein the amount of bromide ions to be added is in the range of 0.002 to 0.1 g/l.
14. The acidic cleaning aqueous solution for an aluminum-based metal according to Claim 12, wherein the amount of the polyhydric alcohol to be added is in the range of 0.1 to 5 g/l.
- 10 15. A method for acidic cleaning an aluminum-based metal which comprises the steps of:

preparing an acidic cleaning aqueous solution containing
at least one selected from inorganic acids in an amount necessary to become pH 2 or less;
oxidizing metal ions;
15 a chelating dispersant; and
a surfactant which may be used in compliance with degreasing requirement, feeding "the oxidizing metal ions and an oxidizing agent" or "the oxidizing agent" to the acidic cleaning aqueous solution, and then measuring an oxidation-reduction potential of the aqueous solution to maintain and control the concentration of the oxidizing metal ion in the aqueous solution.
20 16. The method for acidic cleaning an aluminum-based metal according to Claim 15, wherein the oxidizing metal ions are ferric ions, metavanadic ions or cerium(IV) ions.
17. The method for acidic cleaning an aluminum-based metal according to Claim 15, wherein
25 the oxidizing metal ions are contained in an amount of 0.05 to 4 g/l in the acidic aqueous solution.
18. The method for acidic cleaning an aluminum-based metal according to Claim 15, wherein the inorganic acid is sulfuric acid or nitric acid.
30 19. The method for acidic cleaning an aluminum-based metal according to Claim 15, wherein a pH of the acidic cleaning aqueous solution is in the range of 0.6 to 2.
20. The method for acidic cleaning an aluminum-based metal according to Claim 15, wherein the chelating dispersant is a phosphonic acid compound.
35 21. The method for acidly cleaning an aluminum-based metal according to Claim 15, wherein the chelating dispersant is at least one phosphonic acid compound selected from the group consisting of 1-hydroxyethylidene-1,1-disphosphonic acid, aminotri(methylenephosphonic acid) and ethylenediaminetetra(methylenephosphonic acid).
40 22. The method for acidic cleaning an aluminum-based metal according to Claim 15, wherein the chelating dispersant is contained in an amount of 0.05 to 5 g/l in the acidic aqueous solution.
23. The method for acidic cleaning an aluminum-based metal according to Claim 15, wherein
45 the surfactant is at least one nonionic surfactant selected from the group consisting of ethoxylated alkylphenols, hydrocarbon derivatives and abietic acid derivatives.
24. The method for acidic cleaning an aluminum-based metal according to Claim 15, wherein the surfactant is contained in an amount of 0.1 to 10 g/l in the acidic aqueous solution.
50 25. The method for acidic cleaning an aluminum-based metal according to Claim 15, further having bromide ions and/or a polyhydric alcohol added.
26. The method for acidic cleaning an aluminum-based metal according to Claim 25, wherein
55 the amount of the bromine ions to be added is in the range of 0.002 to 0.1 g/l.
27. The method for acidic cleaning an aluminum-based metal according to Claim 25, wherein the amount of the polyhydric alcohol to be added is in the range of 0.1 to 5 g/l.

28. The method for acidic cleaning an aluminum-based metal according to Claim 15, wherein an oxidation-reduction potential (the ORP) of an acidic cleaning bath is in the range of 0.55 to 0.7 (vs. Ag/AgCl).

5 29. The method for acidic cleaning an aluminum-based metal according to Claim 15, wherein an oxidizing agent is H₂O₂.

Amended claims under Art. 19.1 PCT

10 1. An acidic cleaning aqueous solution for an aluminum-based metal which comprises:

an inorganic acid in an amount necessary to become pH 2 or less;
oxidizing metal ions; and
a chelating dispersant consisting essentially of a phosphonic acid compound.

15 2. An acidic cleaning aqueous solution for an aluminum-based metal which comprises:

an inorganic acid in an amount necessary to become pH 2 or less;
oxidizing metal ions;
20 a chelating dispersant consisting essentially of a phosphonic acid compound; and
a surfactant.

25 3. The acidic cleaning aqueous solution for an aluminum-based metal according to Claim 1 or 2, wherein the oxidizing metal ions are ferric ions, metavanadic ions or cerium(IV) ions.

4. The acidic cleaning aqueous solution for an aluminum-based metal according to Claim 1 or 2, wherein the oxidizing metal ions are contained in an amount of 0.05 to 4 g/l in the acidic aqueous solution.

30 5. The acidic cleaning aqueous solution for an aluminum-based metal according to Claim 1 or 2, wherein the inorganic acid is sulfuric acid or nitric acid.

6. The acidic cleaning aqueous solution for an aluminum-based metal according to Claim 1 or 2, wherein a pH of the acidic cleaning aqueous solution is in the range of 0.6 to 2.

35 7. The acidic cleaning aqueous solution for an aluminum-based metal according to Claim 1 or 2, wherein the chelating dispersant is at least one phosphonic acid compound selected from the group consisting of 1-hydroxyethylidene-1,1-diphosphonic acid, aminotri(methylenephosphonic acid) and ethylenediaminetetra(methylenephosphonic acid).

40 8. The acidic cleaning aqueous solution for an aluminum-based metal according to Claim 1 or 2, wherein the chelating dispersant is contained in an amount of 0.05 to 5 g/l in the acidic aqueous solution.

45 9. The acidic cleaning aqueous solution for an aluminum-based metal according to Claim 1 or 2, wherein the surfactant is at least one nonionic surfactant selected from the group consisting of ethoxylated alkylphenols, hydrocarbon derivatives and abietic acid derivatives.

10. The acidic cleaning aqueous solution for an aluminum-based metal according to Claim 1 or 2, wherein the surfactant is contained in an amount of 0.1 to 10 g/l in the acidic aqueous solution.

50 11. The acidic cleaning aqueous solution for an aluminum-based metal according to Claim 1 or 2, further having a bromide ions and/or a polyhydric alcohol added.

12. The acidic cleaning aqueous solution for an aluminum-based metal according to Claim 11, wherein the amount of bromide ions to be added is in the range of 0.002 to 0.1 g/l.

55 13. The acidic cleaning aqueous solution for an aluminum-based metal according to Claim 11, wherein the amount of the polyhydric alcohol to be added is in the range of 0.1 to 5 g/l.

14. A method for acidic cleaning an aluminum-based metal which comprises the steps of:

preparing an acidic cleaning aqueous solution containing
 at least one selected from inorganic acids in an amount necessary to become pH 2 or less;
 oxidizing metal ions;
 a chelating dispersant consisting essentially of a phosphonic acid compound; and
 a surfactant which may be used in compliance with degreasing requirement, feeding "the oxidizing metal ions
 and an oxidizing agent" or "the oxidizing agent" to the acidic cleaning aqueous solution, and then
 measuring an oxidation-reduction potential of the aqueous solution to maintain and control the concentration
 of the oxidizing metal ion in the aqueous solution.

15. The method for acidic cleaning an aluminum-based metal according to Claim 14, wherein
 the oxidizing metal ions are ferric ions, metavanadic ions or cerium(IV) ions.
16. The method for acidic cleaning an aluminum-based metal according to Claim 14, wherein
 the oxidizing metal ions are contained in an amount of 0.05 to 4 g/l in the acidic aqueous solution.
17. The method for acidic cleaning an aluminum-based metal according to Claim 14, wherein
 the inorganic acid is sulfuric acid or nitric acid.
18. The method for acidic cleaning an aluminum-based metal according to Claim 14, wherein
 a pH of the acidic cleaning aqueous solution is in the range of 0.6 to 2.
19. The method for acidly cleaning an aluminum-based metal according to Claim 14, wherein
 the chelating dispersant is at least one phosphonic acid compound selected from the group consisting of 1-
 hydroxyethylidene-1,1-disphosphonic acid, aminotri(methylenephosphonic acid) and ethylenediaminetetra(methyl-
 enephosphonic acid).
20. The method for acidic cleaning an aluminum-based metal according to Claim 14, wherein
 the chelating dispersant is contained in an amount of 0.05 to 5 g/l in the acidic aqueous solution.
21. The method for acidic cleaning an aluminum-based metal according to Claim 14, wherein
 the surfactant is at least one nonionic surfactant selected from the group consisting of ethoxylated alkylphe-
 nols, hydrocarbon derivatives and abietic acid derivatives.
22. The method for acidic cleaning an aluminum-based metal according to Claim 14, wherein
 the surfactant is contained in an amount of 0.1 to 10 g/l in the acidic aqueous solution.
23. The method for acidic cleaning an aluminum-based metal according to Claim 14, further having bromide ions
 and/or a polyhydric alcohol added.
24. The method for acidic cleaning an aluminum-based metal according to Claim 23, wherein
 the amount of the bromine ions to be added is in the range of 0.002 to 0.1 g/l.
25. The method for acidic cleaning an aluminum-based metal according to Claim 23, wherein
 the amount of the polyhydric alcohol to be added is in the range of 0.1 to 5 g/l.
26. The method for acidic cleaning an aluminum-based metal according to Claim 14, wherein
 an oxidation-reduction potential (the ORP) of an acidic cleaning bath is in the range of 0.55 to 0.7 (vs.
 Ag/AgCl).
27. The method for acidic cleaning an aluminum-based metal according to Claim 14, wherein
 an oxidizing agent is H₂O₂.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP95/01171

A. CLASSIFICATION OF SUBJECT MATTER		
Int. Cl ⁶ C23G1/12, C23F1/20		
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)		
Int. Cl ⁶ C23G1/12, C23F1/20		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Jitsuyo Shinan Koho 1926 - 1995		
Kokai Jitsuyo Shinan Koho 1971 - 1995		
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.
X	JP, 3-65436, B2 (Nippon Paint Co., Ltd.), October 11, 1991 (11. 10. 91), Lines 1 to 17, column 1, line 14, column 3 to line 7, column 4, lines 20 to 29, column 5, lines 38 to 44, column 6 & US, 4851148, A & CA, 1275378, A1 & AU, 582226, B2 & AT, 38397, E & EP, 196668, B1	1 - 6, 10 - 11, 15 - 19, 23 - 24, 28 - 29
Y	JP, 3-65436, B2 (Nippon Paint Co., Ltd.), October 11, 1991 (11. 10. 91), Lines 1 to 17, column 1, line 14, column 3 to line 7, column 4, lines 20 to 29, column 5, lines 38 to 44, column 6 & US, 4851148, A & CA, 1275378, A1 & AU, 582226, B2 & AT, 38397, E & EP, 196668, B1	7 - 9 12, 14, 20 - 22, 25, 27
Y	JP, 4-52289, A (Nihon Parkerizing Co., Ltd.), February 20, 1992 (20. 02. 92), Line 5, left column to line 14, right column, page 1, line 17, lower left column to line 1, lower right column, page 2, lines 9 to 12,	12, 14, 25, 27
☒ 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 "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "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
August 28, 1995 (28. 08. 95)		September 12, 1995 (12. 09. 95)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP95/01171

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	lower left column, page 3 & WO, 9119830, A1 & AU, 8052491, A1	

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