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(54) Method of pickling aluminium can bodies

(57) This invention provides a method of pickling an aluminum can body comprising ejecting a pickling agent from a tank against an aluminum can body caused to traverse said tank overhead to clean them and recycling the used agent to said tank,

wherein said pickling agent is an acidic aqueous solution containing (A) a polyethylene glycol type detergent nonionic surfactant having an HLB value of 14 to 18 and (B) a low-foaming nonionic surfactant having an HLB value of 2 to 12,
the concentration of (A) is 100 to 5000 ppm and the ratio of (A) to (B) is 10:90 to 90:10, and
the pickling agent in the tank is withdrawn out of the system from below the agent level.

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Description

FIELD OF THE INVENTION

[0001] The present invention relates to a method of cleaning aluminum can bodies for beverage or other uses and more particularly to a pickling method suited for pretreatment preceding a chemical conversion or other treatment of aluminum can bodies.

PRIOR ART

[0002] Aluminum cans for beverage use which are made of aluminum or an aluminum alloy are generally manufactured by a drawing process called drawing and ironing (DI). The aluminum cans just produced by this process carry fine aluminum particles (smuts) shaven off the material on drawing as well as the lubricating oil. Therefore, in order that chemical conversion treatment or coating may be effected to such aluminum cans, the cans must be cleaned of such smut and lubricating oil in advance.

[0003] For the surface cleaning of aluminum cans, a hydrofluoric acid type pickling agent or a fluorine-free pickling agent, which etches the metal surface in an appropriate degree and thereby cleans the cans, is generally employed. Moreover, in such pickling agents, surfactants with HLB values smaller than 14 are generally used. In addition, to prevent an excessive accumulation of oil in the pickling agent and consequent decrease in degreasing power of the agent, it is a prevailing practice to remove the pickling agent from the system to control the concentration of oil in the pickling agent below a certain level. This removal of the agent from the system is generally effected by allowing the agent to overflow the top of a cleaning tank.

[0004] The problem which arises when the maintenance of wholesomeness of the pickling agent is sought by the above overflowing system is that a part of the surfactant having an affinity for lubricating oil is removed together with the oil floating on the liquid surface from the system. If, to overcome this disadvantage, the spray pipeline is utilized to draw out the washing agent from the tank at a relatively low level, the oil floating at the liquid level cannot be removed but is entrained into spray mists and ejected against the aluminum can bodies. The resulting residue of lubricating oil on the can surface interferes with the formation of a chemical conversion film and tends to cause black discoloration of the can bottom in the stage of sterilizing the filled cans.

SUMMARY OF THE INVENTION

[0005] The object of the present invention, therefore, is to provide a method for pickling an aluminum can body which makes full use of the surfactant component of a pickling agent and provides for steady cleaning with good reproducibility.

[0006] The method of pickling an aluminum can body

comprises ejecting a pickling agent from a tank against an aluminum can body caused to traverse said tank overhead to clean them and recycling the used agent to said tank,
wherein said pickling agent is an acidic aqueous solution containing (A) a polyethylene glycol type detergent nonionic surfactant having an HLB value of 14 to 18 and (B) a low-foaming nonionic surfactant having an HLB value of 2 to 12,
the concentration of (A) is 100 to 5000 ppm and the ratio of (A) to (B) is 10:90 to 90:10, and
the pickling agent in the tank is withdrawn out of the system from below the agent level.

[0007] An exemplary mode of said withdrawal of the pickling agent from the system below the surface of the body of agent may comprise drawing out the pickling agent from the tank through a spray piping, discarding a portion of the drawn agent out of the system and ejecting the remainder in a mist form against an aluminum can body to clean them and recycling the used agent to the tank.

DETAILED DESCRIPTION OF THE INVENTION

[0008] The method of the present invention is now described in detail.

[0009] Referring to Fig. 1 which is a schematic diagram illustrating an embodiment of the pickling method of the present invention, a tank 1 contains a prepared pickling agent 2. For cleaning can bodies, the pickling agent 2 is drawn out of the tank 1 by a pump 3 and fed to risers 5 via a spray pipeline 4 branching into a line extending horizontally over the cans and a line extending horizontally below the cans. Though not accurately depicted, the risers 5 are disposed at right angles with the spray pipeline 4 and provided with a plurality of can-cleaning spray nozzles 6. The position where pickling agent 2 is drawn off from tank 1 is not particularly restricted as far as it is below the agent level. There

can be mentioned near the agent level, side bottom of the tank and bottom of the tank, preferably side bottom of the tank and bottom of the tank.

[0010] On the other hand, aluminum can bodies 7 are arranged with their open sides down on a conveyer belt 8 made of acid-resistant material and, as such, traverse over the tank 1. The smut and lubricating oil adherent to the can bodies 7 are flushed off by the jets of pickling agent 2 delivered from the nozzles 6 in the upper and lower rows. Preferably, the pickling agent is warmed to 35 to 85 °C, more preferably 50 to 80 °C, in advance, and ejected over a time of preferably 30 to 300 seconds, more preferably 45 to 120 seconds. The system is so designed that the used agent is recycled to the tank 1.

[0011] As the cleaning of aluminum can bodies 7 is repeated, the oil accumulates gradually in the pickling agent 2 in the tank 1. To continue cleaning while this oily impurity is removed, the pickling agent 2 withdrawn through the spray pipeline 4 may be discharged from the system through a drain branch pipe 9. As an alternative, a drain port other than said drain pipe 9 may be provided in the lower side wall or bottom of the tank 1 to withdraw the agent through the port as needed.

[0012] The pickling agent 2 for use in the present invention contains a polyethylene glycol type detergent nonionic surfactant (A) having an HLB value of 14 to 18 and a low-foaming nonionic surfactant (B) having an HLB value of 2 to 12. The concentration of the detergent nonionic surfactant (A) in the agent is 100 to 5000 ppm, preferably 1000 to 3000 ppm, and the HLB value of (A) is 14 to 18, preferably 15 to 17. As the detergent nonionic surfactant (A), an alkyl alcohol ethylene oxide adduct is most preferred but an alkylphenol ethylene oxide adduct and an abietic acid derivative, for instance, can also be employed. When the concentration amount of the detergent nonionic surfactant (A) is lower than 100 ppm, the degreasing power of the agent is insufficient so that the formation of a chemical conversion film is rendered difficult and a black discoloration of the can bottom is induced in the heat-sterilization of filled cans. Use of (A) in excess of 5000 ppm will not be rewarded with any further improvement in degreasing power but rather will induce copious foaming in the tank.

[0013] On the other hand, the HLB value of the low-foaming nonionic surfactant (B) is 2 to 12, preferably 5 to 9. The low-foaming nonionic surfactant (B) is added for defoaming purposes and, as such, various known surfactants can be employed. As examples, there can be mentioned the ethylene oxide adduct, propylene oxide adduct, and ethylene oxide/propylene oxide adduct of an alkyl alcohol or alkylphenol, an abietic acid derivative, or a mixture thereof. Furthermore, the ratio of (A) to (B) is 10:90 to 90:10, preferably 30:70 to 60:40. When the ratio of (A) is smaller than 10, the lipophilicity of the nonionic surfactant as a whole is so high that the lubricating oil mixing in the pickling agent on the cleaning of cans is coupled to the surfactant and floats on the surface of the body of agent in the tank. This oil cannot be effectively removed from a level below the liquid surface, with the result that the cleaning power is decreased. On the other hand, when the ratio of (A) exceeds 90, the foaming of the pickling agent in the tank becomes too vigorous to be easily controlled.

[0014] It is essential of the pickling agent for use in the present invention to contain said detergent nonionic surfactant (A) having a comparatively high hydrophilicity of HLB 14 to 18. This surfactant has a high capacity to emulsify the lubricating oil contaminating the pickling agent on the cleaning cans and, therefore, unlike the conventional washing agent with an HLB value of less than 14, it does not couple with the lubricating oil and cause it to float on the surface of the body of agent but gives a generally uniform dispersion in the tank. Therefore, the pickling agent pumped up to the nozzles contains the detergent nonionic surfactant (A) retaining a sufficient degreasing power.

[0015] The pickling agent contains not only said nonionic surfactants but also an inorganic acid such as nitric acid, sulfuric acid, phosphoric acid or the like. With such an inorganic acid, the pickling agent is adjusted to, for example, an acidity of not over pH 2, preferably pH 0.6 to 2. Among other components which may also be formulated is an etching agent such as oxidation-form metal ions such as ferric ion (Fe^{3+}), ceric ion (Ce^{4+}), cobaltic ion (Co^{3+}), stannic ion (Sn^{4+}), etc. and oxidation-form metal oxoanions such as metavanadate ion (VO^{3-}). The preferred amount of the etching agent in the pickling agent is 0.02 to 0.4 mass %.

[0016] To uphold the activity of said etching agent, it is good practice to supplement the pickling agent with an oxidizing agent such as hydrogen peroxide (H_2O_2), a persulfate salt (e.g. $NaS_2O_3^{2-}$), ozone (O_3), a cerium compound [e.g. cerium ammonium sulfate $(NH_4)_4Ce(SO_4)_4$] or a nitrite salt (e.g. $NaNO_2$, KNO_2, etc.).

[0017] To prevent decomposition of the surfactant by the oxidizing agent, a polyhydric alcohol having at least 2 hydroxyl groups directly attached to adjacent carbon atoms of the backbone chain can be added. As examples, 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. can be mentioned. The preferred level of said polyhydric alcohol in the pickling agent is 0.01 to 0.5 mass %.

[0018] As mentioned above, when only a surfactant with an HLB value of less than 14 is used, it tends to float on the surface of the body of surfactant by its own nature. Therefore, the conventional overflow system was sometimes inadequate in degreasing power because a substantial amount of the surfactant is removed together with the oil to reduce the surfactant concentration of the pickling agent. However, in accordance with the method of the present

invention, the pickling agent is withdrawn from a level below the surface of the body of agent so that the surfactant concentration of the pickling agent can be held high and the decrease in degreasing power of the agent can be prevented.

[0019] In the method of pickling an aluminum can body of the present invention, since a pickling agent comprises (A) a polyethylene glycol type detergent nonionic surfactant having an HLB value of 14 to 18, said pickling agent has affinity for the lubricating oil contaminating the agent on the cleaning cans and that for water in the tank. Further, said agent comprises (B) a low-foaming nonionic surfactant having an HLB value of 2 to 12 at a specific ratio to the surfactant (A) , said pickling agent does not show an excessive form.

[0020] Therefor, in the method of pickling an aluminum can body of the invention, significant surfactants do not float on the agent surface together with oils as the conventional washing agents comprising only the surfactants having an HLB value of lower than 14 and surfactants are dispersed in the tank uniformly. Accordingly, the pickling agent delivered from the nozzles contains the surfactants having sufficient degreasing power.

EXAMPLES

[0021] The following working and comparative examples illustrate the present invention in further detail.

Example 1

[0022]

(1) Substrate

Lid-free can bodies carrying lubricating oil and smut as obtained by DI processing of a 3004 aluminum alloy sheet were used.

(2) Pickling agent

A fluorine-free pickling agent containing, as the detergent nonionic surfactant (A) having an HLB value of 16.9, 1500 ppm of a straight-chain alkyl alcohol (C_{12} to C_{16} mixture)-ethylene oxide adduct and, as the low-foaming nonionic surfactant (B) having an HLB value of 6.2, 1500 ppm of a straight-chain alkyl alcohol (C_{12} to C_{16} mixture)-ethylene oxide/propylene oxide adduct (A:B = 50:50; Propylene oxides were calculated as hydrophobic groups when HLB values were obtained), and as the inorganic acid, 20000 ppm of sulfuric acid was used.

(3) Treating conditions

The above can bodies were pickled with the equipment shown schematically in Fig. 1. In this operation, a portion of the agent to be recycled was withdrawn from the spray pipeline at the rate of 180 l/h, while a fresh pickling agent was added to the tank at the rate of 360 l/h, in taking into account the amount carried over as adhered to the can bodies and conveyer belt. In this manner, can bodies were treated continuously at the rate of 80000 cans/hr for 72 hours. The temperature of the pickling agent was 70 °C and the treating time (spray time) was 50 seconds. After pickling, the can bodies were rinsed with tap water for 15 seconds and further treated with a chemical conversion reagent composition ("Alsurf 440", Nippon Paint) at 40 °C for 12 seconds. The above operation was followed by spray-washing with tap water for 15 seconds and deionized water for 5 seconds and further by drying at 190 °C for 3 minutes.

(4) Evaluation

The pickling agent composition after completion of the pickling operation was analyzed by Cesibor titrimetry for the concentration of the surfactant and a TOC (total organic carbon) meter ("TOC 5000", Shimadzu Corporation) for oil. As a result, the surfactant concentration and the oil fraction were found to be remaining steady at 2500 ppm and 1000 ppm, respectively. From among the treated can bodies, 3 cans were randomly sampled and the bottom was cut out from each sample and immersed in tap water at 100 °C for 30 minutes to evaluate the boiling water resistance. As a result, there was no blackening of the outer surface of the can bottom.

Examples 2 to 9

[0023] Except that the kind of pickling agent, treating temperature or the species or HLB value of nonionic surfactants (A) and (B) were varied as shown in Table 1, the procedure of Example 1 was otherwise repeated to treat can bodies and examine the bottoms of the treated cans. The results are shown in Table 1.

Comparative Example 1

[0024] Except that a fluorine-free pickling agent containing 1500 ppm of a nonionic surfactant having an HLB value of 13, namely a straight-chain alkyl alcohol (C_{12} to C_{16} mixture)-ethylene oxide adduct, was used in lieu of the pickling agent used in Example 1, the procedure of Example 1 was otherwise repeated to treat can bodies. With regard to the tank composition after treatment, the concentration of the nonionic surfactant and that of the oil fraction had decreased to 1500 ppm and 500 ppm, respectively. Moreover, a brown oil (grease) was found afloat on the agent surface of the cleaning solution in the tank. Evaluation of the can bodies after chemical conversion treatment as in Example 1 revealed punctate blackening of the outer surface of the can bottom.

Table 1

No.	Pickl-ing agent	Pickl-ing temp. (°C)	Nonionic surfactant (A)		Nonionic surfactant (B)		Surfactant (A+B)		Conc. of oil after treat-ment (ppm)	Boiling water resist-ance
			HLB	Species*1	HLB	Species*2	Initial Conc.*3 (ppm)	Conc. after treat-ment*3 (ppm)		
Ex. 1	F-free	70	16.9	a	6.2	a	3000	2500	1000	Not tarnished
Ex. 2	F-free	70	16.9	b	6.2	a	3000	2400	1000	Not tarnished
Ex. 3	F-free	70	15.4	a	6.2	a	3000	2500	900	Not tarnished
Ex. 4	F-free	70	16.9	a	6.2	a	2000	1700	700	Not tarnished
Ex. 5	F-free	80	16.9	a	6.2	a	3000	2400	1200	Not tarnished
Ex. 6	F-free	70	16.9	c	6.2	a	3000	2500	1000	Not tarnished
Ex. 7	F-free	70	16.9	a	7.8	a	3000	2600	1000	Not tarnished
Ex. 8	F-free	70	16.9	a	6.2	b	3000	2400	1100	Not tarnished
Ex. 9	F-con-taining*4	55	14.3	a	6.2	a	3000	2600	1100	Not tarnished
Compar. Ex. 1	F-free	70	13.0	a	6.2	a	3000	1500	500	Punctate blacken-

*1 The species of nonionic surfactant (A) were as follows.
a··· a straight-chain alkyl alcohol (C_{12} to C_{15} mixture)-ethylene oxide adduct
b··· a branched-chain alkyl alcohol (C_{12} to C_{15} mixture)-ethylene oxide adduct
c··· an alkylphenol-ethylene oxide adduct

*2 The species of nonionic surfactant (B) were as follows.
a··· a straight-chain alkyl alcohol (C_{12} to C_{15} mixture)-ethylene oxide/propylene oxide adduct
b··· a branched-chain alkyl alcohol (C_{12} to C_{16} mixture)-ethylene oxide/propylene oxide adduct

*3 The combined concentration of nonionic surfactant (A) and nonionic surfactant (B). A:B (1:1).

*4 Pickling agent at pH 1.3, which contains, in addition to the nonionic surfactants (A) and (B), 10000 ppm of sulfuric acid and 20 ppm of hydrofluoric acid.

Claims

1. A method of pickling an aluminum can body

comprising ejecting a pickling agent from a tank against an aluminum can body caused to traverse said tank overhead to clean them and recycling the used agent to said tank,
wherein said pickling agent is an acidic aqueous solution containing (A) a polyethylene glycol type detergent nonionic surfactant having an HLB value of 14 to 18 and (B) a low-foaming nonionic surfactant having an HLB value of 2 to 12,
the concentration of (A) is 100 to 5000 ppm and the ratio of (A) to (B) is 10:90 to 90:10, and
the pickling agent in the tank is withdrawn out of the system from below the agent level.

2. The method of pickling an aluminum can body according to Claim 1
wherein said detergent nonionic surfactant (A) is an alkyl alcohol-ethylene oxide adduct.

3. The method of pickling an aluminum can body according to Claim 1 or 2
wherein said low-foaming nonionic surfactant (B) is an alkyl alcohol-ethylene oxide adduct and/or -propylene oxide adduct.

4. The method of pickling an aluminum can body according to any of Claims 1 to 3
comprising withdrawing the pickling agent in the tank via a spray pipeline, removing a portion of the withdrawn

pickling agent out of the system, ejecting the balance against an aluminum can body to clean them, and recycling the waste agent to the tank.

5. An aluminum can body obtainable by pickling it using the method according to any of Claims 1 to 4.

Fig. 1