

COMPOSITIONS AND PROCESSES FOR TREATING
TIN-PLATED STEEL SURFACES

5 The present invention relates to compositions and processes for treating tin-plated steel surfaces. It is more particularly concerned with liquid surface-treatment compositions and processes in which they are employed to treat the surfaces of drawn and ironed (hereinafter "DI") tin cans.

10 The purpose of the compositions and processes herein disclosed is to impart excellent corrosion-resistance and paint-adherence properties to the surface of such DI cans after their formation by the draw-ironing of tin-plated steel sheet but before its painting or printing, and indeed also to impart to their surfaces the low coefficient of friction (below for simplicity designated simply as "slideability")
15 which is required for the smooth conveyor-transportation of such cans.

Liquid compositions for treating the surface of tin-plated DI cans to improve their corrosion-resistance or their slideability are, of course, already known - but they are not free from problems.
20

Thus for example in (1) Japanese Patent Application Laid Open [Kokai or Unexamined] Number Hei 01-100,281 [100,281/90] there is disclosed a film-forming liquid composition for the treatment of metal surfaces, in which the liquid composition has a pH of
25 from 2 to 6 and contains from 1 to 50 g/L of phosphate ion, from 0.2 to 20.0 g/L of oxyacid ion, from 0.01 to 5.0 g/L of tin ion, and from 0.01 to 5.0 g/L of condensed phosphate ion. This known liquid composition can be used to form a corrosion-resistant phosphate
30 film on the surface of tin-plated DI cans - but unfortunately it cannot nowadays meet the need for surface treatments which import a far better corrosion-

resistance than before, which has been forced on manufacturers as the tin-plated DI can produced over the last few years has carried smaller quantities of tin plating in response to economic pressures.

5 Another known composition for improving corrosion resistance is that disclosed in (2) Japanese Patent Application Laid Open Number Hei 01-172,406 [172,406/89] which utilizes a suitable polyhydric phenol compound as a water-soluble resin to improve the
10 corrosion-resistance and paint-adherence upon metal surfaces treated with an aqueous solution thereof. This procedure however does not always reliably yield a satisfactory degree of corrosion resistance when treating tin-plated DI cans by this method.

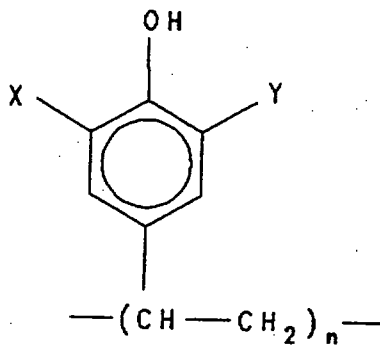
15 Liquid compositions are also already known for improving slideability. This is desirable, since if the exterior of a metal can has a high friction coefficient this may lead to manufacturing problems, as it causes the can surface to have a poor slideability
20 during conveyor transportation thereof, and this in turn often causes the can to tumble over sideways and thus interfere with the transport operation. Transportability of the can in the correct attitude is of particular importance when it is to be delivered to
25 a printer - and it is therefore necessary in the can-manufacturing industry to reduce the static friction coefficient of the exterior can surface without impairing the adherence of any paint or lacquer to be coated onto the can during the printing operation.

30 An agent for treating the surfaces of metal cans to improve their slideability has been disclosed in (3) Japanese Patent Application Laid Open Number Sho 64-85292 [85,292/89] which describes the use for this purpose of water-soluble organic material selected from
35 phosphate esters, alcohols, monovalent and polyvalent fatty acids, fatty acid derivatives, and mixtures

thereof. However, although the use of the agent disclosed in document (3) does indeed improve the slideability of the cans to a certain extent, unfortunately it does not significantly improve the corrosion-resistance or paint-adherence of tin-plated DI cans.

It is therefore the aim of this invention to achieve the much needed but hitherto-unattained objective, in the treatment of tin-plated DI cans, of providing a liquid treatment composition which not only (a) forms a film which simultaneously provides excellent corrosion-resistance, paint-adherence and slideability, but also (b) displays excellent processing characteristics so that it will be capable of supporting continuous treatment.

According to one aspect of the present invention there is therefore provided an aqueous liquid composition for treating the surface of tin-plated DI cans, said liquid composition having a pH of 2.0 to 6.5 and which besides water includes from 1 to 30 grams per litre (hereinafter "g/L") of phosphate ions, from 0.1 to 5 g/L of condensed phosphate ions, from 0.5 to 5 g/L of reducing agent, and from 0.1 to 20 g/L (as dissolved solids) of one or more water-soluble resin(s) being a polymer substantially consisting of monomeric units conforming to the general formula:

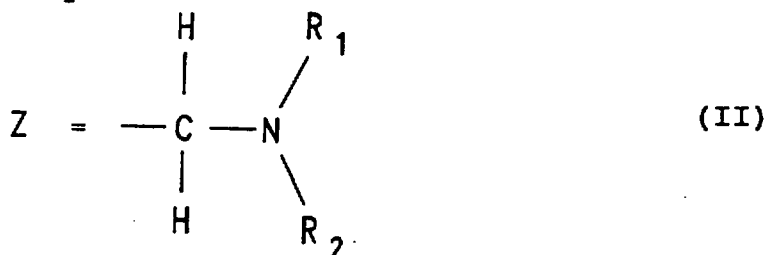


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wherein:

n is an integer with a value in the range from 2 to 80 for individual monomeric units in the resin but may

have a non-integral average value for the resin component as a whole; and X and Y, independently of each other and independently for each monomeric unit, each represents either an hydrogen atom or a group "Z" conforming to the general formula:



(in which R_1 and R_2 , independently of each other and independently for each Z group in the monomeric unit, each represents a C_1 to C_{10} alkyl and/or hydroxyalkyl moiety);
provided that the total number of Z groups present in the resin component is in the range of from 30 to 200% of the total number of aromatic rings in the resin component.

While the presence of other components is not wholly debarred, we are aware of no advantage to be gained thereby, and it preferred that the components specified above shall be the only ones.

This liquid composition for treating the surface of tin-plate DI cans forms a film which simultaneously provides excellent corrosion-resistance, paint-adherence and slideability, and it also has excellent processing characteristics which make continuous treatment possible.

The phosphate ions in the liquid composition can be provided by phosphoric acid (H_3PO_4), sodium phosphate (Na_3PO_4) or other sources of phosphate ion. The concentration of phosphate ions should be in the range of from 1 to 30 g/L. At phosphate ion

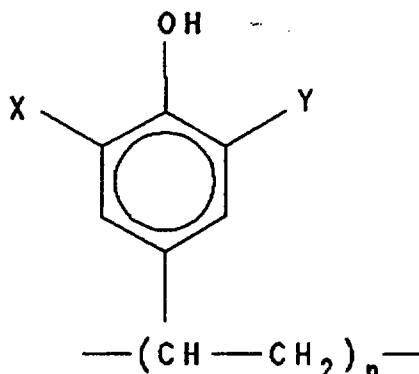
concentrations below 1 g/L the reactivity is poor and film formation will not usually be satisfactory. While a good-quality film can be formed at values in excess of 30 g/L, the cost of the liquid composition is thereby increased and thus the economic value is impaired. The preferred phosphate ion concentration is in the range of from 5 to 15 g/L.

The condensed phosphate ions in the liquid composition may be pyrophosphate ions, tripolyphosphate ions and/or tetrapolyphosphate ions. They may be introduced into the composition in any convenient manner, e.g.. as the free acid or as a salt. Thus, for example, pyrophosphate ion may be introduced in the form of pyrophosphoric acid ($\text{H}_4\text{P}_2\text{O}_7$), sodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7$) or other salts. The condensed phosphate ion component should be present in a concentration in the range of from 0.1 to 5 g/L. At values less than 0.1 g/L, a satisfactory film will not normally be formed, due to the weak etching activity; but on the other hand, the etching activity is too high at condensed phosphate ion concentrations in excess of 5 g/L, and the film-forming reaction is usually inhibited. The preferred concentrations are in the range of from 0.4 to 1 g/L.

The reducing agent is not specifically restricted, but it preferably consists of phosphorous acid and/or hypophosphorous acid, and/or salts of these acids. While its appropriate concentrations will be governed by the reducing power of the particular reducing agent, the general range of 0.5 to 5 g/L is preferred. At concentrations of less than 0.5 g/L, a satisfactory effect is often not developed by this component due to the weak reducing activity. The cost of the treatment liquid composition is increased and the economics become problematical at reducing agent concentrations in excess of 5 g/L. As an example, the acid or salt can be used to

introduce phosphorous acid or hypophosphorous acid, and their preferred addition is 1 to 3 g/L, measured as the stoichiometric equivalent as acid.

The water soluble resin used by the present invention comprises polymer with the following general formula:



in which n has a value of 2 to 80. The molecular weight is too low at values of n below 2 and no improvement in corrosion resistance for the treated tin plate will normally be observed. At values of $n = 81$ and above, the aqueous solution has a reduced stability which will normally generate problems in practical use.

The groups R_1 and R_2 in the general formula for the groups Z already given above are C_1 to C_{10} alkyl and/or hydroxyalkyl groups. Functional groups containing 11 or more carbons reduce the stability of the aqueous solution. The group Z is preferably $-CH_2N(CH_3)CH_2CH_2OH$ or $-CH_2N(CH_3)_2$.

The number of groups Z should be 30 to 200 % of the number of aromatic rings in the above-described resin polymer. Thus, when five Z groups are present in a polymer with $n = 10$, the ratio of Z 's to aromatic rings is then 50 %. Ratios below 30 % cause the resin to be poorly water soluble and thus risk stability problems. (Ratios higher than 200 % would be inconsistent with the general formula for the resin.)

The specified water soluble resin should be present at 0.1 to 20 g/L on a solids basis. Resin concentrations less than 0.1 g/L make stable film formation on the can surface

highly problematic. Concentrations in excess of 20 g/L are uneconomical due to the increased cost of the treatment solution.

5 The pH of the treatment liquid composition must be in
the range from 2.0 to 6.5. Etching is heavy and film formation is impaired at pH values less than 2.0. At pH values in excess of 6.5, the liquid composition life is shortened because the resin tends to precipitate and sediment. The pH can be adjusted as needed through the use of an
10 acid, for example, phosphoric acid, nitric acid, hydrochloric acid, hydrofluoric acid, or the like, or through the use of a base, for example, sodium hydroxide, sodium carbonate, ammonium hydroxide, or the like.

15 The method for preparing the surface-treatment liquid composition according to the present invention can be briefly explained as follows. Prescribed quantities of phosphate ions, condensed phosphate ions, and reducing agent as described above are dissolved in water with thorough stirring. When the pH of this liquid composition is
20 not already less than 7, it is adjusted to below 7 using the appropriate acid as listed above. The water soluble resin specified by the present invention is then added and completely dissolved while stirring, and the pH is adjusted as discussed above if not already within the desired range.

25 The film which is formed by contact of the surface treatment liquid composition of the present invention with tin plate is an organic/inorganic composite film which is composed of the resin and phosphate salts, with the main component of the phosphate salts being tin phosphate. The
30 substrate is etched by the phosphate ion and condensed phosphate ion, the pH at this time is locally increased at the interface, and phosphate salt is deposited on the surface. Moreover, the amino groups in the resin have a chelating activity, and probably form a coordination compound
35 with the fresh surface of the substrate generated by etching. The organic/inorganic composite film is formed by essentially these two mechanisms. The simultaneous pres-

ence of the condensed phosphate ion probably promotes formation of the resin/metal coordination compound, and this would facilitate the stable formation of the organic/inorganic composite film on the surface over a broad pH range.

5 The process for treating tin-plated DI can using the surface-treatment liquid composition of the present invention will now be considered. The treatment liquid composition can be applied by any method that achieves adequate contact between the liquid composition and the metal surface to be treated for an adequate time. The following process steps constitute a preferred example of a suitable process according to this invention.

1. Surface cleaning of the tin-plated DI can: degreasing
 (a weakly alkaline cleaner is typically used)
- 15 2. Tap water rinse
3. Film-formation treatment (application of the treatment liquid composition according to the present invention)
 treatment temperature: ambient to 80° C
 treatment method: spray
- 20 treatment time: 2 to 60 seconds
4. Tap water rinse
5. Rinse with de-ionized water
6. Drying

 A surface treatment liquid composition according to
25 the present invention can be used at treatment temperatures from room temperature (i.e., about 20° C) up to 80° C; however, it is preferably used generally heated to 40 to 60° C. The contact time should be 2 to 60 seconds. At
30 less than 2 seconds, the reaction is generally inadequate and a highly corrosion resistant film will not be formed. No improvement in performance is observed for treatment times in excess of 60 seconds. Accordingly, the most useful treatment times will fall in the range of 2 to 60 seconds. Contact is preferably by spraying, at least on ob-
35 jects such as tin cans with only one surface plated, in or-

der to avoid waste of treatment materials by unnecessarily treating the unplated side, as would result from immersion contact.

5 The superior utility of the surface-treatment liquid composition according to the present invention will be illustrated in the following through the use of examples and comparison examples.

EXAMPLES AND COMPARISON EXAMPLES

10 General Test Methods and Procedures

The corrosion resistance of treated cans was evaluated using the iron exposure value ("IEV"), and the IEV was measured in accordance with the invention of United States Patent Number 4,332,646. The corrosion resistance is better at lower IEV values, and a score below 150 is generally regarded as excellent.

20 The paint adherence was evaluated based on the peel strength as follows: The surface of the treated can was coated with an epoxy/urea can paint to a film thickness of 5 to 7 micrometers; this was baked at 215° C for 4 minutes; the can was then cut into a 5 x 150 mm strip; a test specimen was prepared by hot-press adhesion with polyamide film; and this was peeled by the 180° peel test method. Accordingly, the paint adherence increases as the peel strength increases, and values in excess of 1.5 kgf/5 mm-width are generally regarded as excellent.

25 The slideability was evaluated by measuring the static friction coefficient of the exterior surface of the can. Thus, the slideability improves as the static friction coefficient declines, and values below 1.0 are generally regarded as excellent.

30 Finally, the stability of the compositions was evaluated as follows. First, tin-plated DI can (manufactured by the DI-processing of tin-plated steel sheet) was degreased using a 1 % hot aqueous solution of a weakly alkaline degreaser (FINECLEANERTM 4361A, commercially supplied by Nihon Parkerizing Company, Ltd.) One immersion cycle consisted

of immersing the degreased can for 2 minutes in 1 L of the particular surface treatment liquid composition heated to 60° C. After 10 cycles, the surface treatment liquid composition was inspected for resin precipitation. The stability was considered to be excellent when resin precipitation was absent.

Example 1

Tin plated DI can was prepared by draw-ironing tin plated steel sheet. It was cleaned with a 1 % hot aqueous solution of a weakly alkaline degreaser (FINECLEANER™ 4361A, registered brand name of Nihon Parkerizing Company, Ltd.), then sprayed with surface-treatment liquid composition 1, heated to 60° C, for 30 seconds, then washed with tap water, sprayed with de-ionized water (with a specific electrical resistance of at least 3,000,000 ohm-cm) for 10 seconds, and, finally, dried in a hot air-drying oven at 180° C for 3 minutes. This treated can was subjected to an evaluation of the corrosion resistance, adherence, and slideability, and the stability of surface-treatment liquid composition 1 was also evaluated.

Surface-treatment liquid composition 1

75% phosphoric acid (H_3PO_4)
10.0 g/L (providing 7.2 g/L of PO_4^{3-} ions)
sodium pyrophosphate ($Na_4P_2O_7 \cdot 10H_2O$)
1.0 g/L (providing 0.4 g/L of $P_2O_7^{4-}$ ions)
phosphorous acid (H_3PO_3)
2.0 g/L (providing 1.9 g/L of PO_3^{3-} ions)
resin solids
2.0 g/L of water soluble resin 1 (see below)
pH = 4.0 (adjusted with sodium hydroxide)
water soluble resin 1 had, in the general formula given above, an average value for n of 40, half the total of X's and Y's in the general formula as Z, and Z was $-CH_2N(CH_3)CH_2CH_2OH$.

Water soluble resin 1 was synthesized as follows. 100 g of propylene glycol monopropyl ether (a CELLOSOLVE™

solvent) was introduced into a 1,000 mL reaction flask equipped with a condenser, nitrogen inlet tube, overhead stirrer, and thermometer, and 60 g of poly-4-vinylphenol (average molecular weight = 5,000) was added and dissolved. 40 g of 2-methylaminoethanol and 100 g of deionized water were added, and this was reacted by heating to 50° C. 40 g of 37 % aqueous formaldehyde solution was added over 1 hour, followed by stirring at 50° C for 2 hours and by stirring for an additional 3 hours at 80° C. The reaction product was cooled, 15 g of 85% orthophosphoric acid was added, and 700 g deionized water was also added. The resin was then precipitated by the addition of 10 % sodium hydroxide solution until the pH of the reaction solution reached 8 to 9. The precipitated resin was filtered off, washed with water, and dried.

Example 2

Tin-plated DI can was cleaned using the same conditions as in Example 1 and was then treated with a 30 second spray of surface treatment liquid composition 2 heated to 60° C. This treatment was followed with a water rinse and drying using the same conditions as in Example 1. The treated can was subjected to an evaluation of the corrosion resistance, adherence, and slideability, and the stability of surface treatment liquid composition 2 was also evaluated.

Surface-treatment liquid composition 2

75% phosphoric acid (H_3PO_4)
10.0 g/L (providing 7.2 g/L of PO_4^{3-} ions)
sodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$)
1.0 g/L (providing 0.4 g/L of $\text{P}_2\text{O}_7^{4-}$ ions)
hypophosphorous acid (H_3PO_2)
2.0 g/L (providing 1.9 g/L of PO_2^{3-} ions)
resin solids
0.4 g/L
pH = 5.0 (adjusted with sodium carbonate)
The water soluble resin was the same as in Example 1.

Example 3

Tin-plated DI can was cleaned using the same conditions as in Example 1 and was then treated with a 30 second spray of surface-treatment liquid composition 3 heated to 60° C. This treatment was followed with a water rinse and drying using the same conditions as in Example 1. This treated can was subjected to an evaluation of the corrosion resistance, adherence, and slideability, and the stability of surface treatment liquid composition 3 was also evaluated.

Surface-treatment liquid composition 3

75% phosphoric acid (H_3PO_4)
20.0 g/L (providing 14.4 g/L of PO_4^{3-} ions)
sodium pyrophosphate ($Na_4P_2O_7 \cdot 10H_2O$)
1.0 g/L (providing 0.4 g/L of $P_2O_7^{4-}$ ions)
phosphorous acid (H_3PO_3)
1.0 g/L (providing 0.96 g/L of PO_3^{3-} ions)
hypophosphorous acid (H_3PO_2)
1.0 g/L (providing 0.95 g/L of PO_2^{3-} ions)
resin solids
8.0 g/L
pH = 4.0 (adjusted with sodium hydroxide)

The water soluble resin was the same as in Example 1.

Example 4

Tin-plated DI can was cleaned using the same conditions as in Example 1 and was then treated with a 30 second spray of surface treatment liquid composition 4 heated to 60° C. This treatment was followed with a water rinse and drying using the same conditions as in Example 1. This treated can was subjected to an evaluation of the corrosion resistance, adherence, and slideability, and the stability of surface-treatment liquid composition 4 was also evaluated.

Surface-treatment liquid composition 4

75% phosphoric acid (H_3PO_4)
15.0 g/L (providing 10.9 g/L of PO_4^{3-} ions)

sodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$)

2.5 g/L (providing 1.0 g/L of $\text{P}_2\text{O}_7^{4-}$ ions)

phosphorous acid (H_3PO_3)

1.0 g/L (providing 0.95 g/L of PO_3^{3-} ions)

5 resin solids

4.0 g/L

pH = 3.0 (adjusted with sodium carbonate)

The water soluble resin was the same as in Example 1.

Example 5

10 Tin-plated DI can was cleaned using the same conditions as in Example 1 and was then treated with a 30 second spray of surface-treatment liquid composition 5 heated to 60° C. This treatment was followed with a water rinse and drying using the same conditions as in Example 1. This
15 treated can was subjected to an evaluation of the corrosion resistance, adherence, and slideability, and the stability of surface-treatment liquid composition 5 was also evaluated.

Surface-treatment liquid composition 5

20 75% phosphoric acid (H_3PO_4)

30.0 g/L (providing 21.6 g/L of PO_4^{3-} ions)

sodium tripolyphosphate ($\text{Na}_5\text{P}_3\text{O}_{10}$)

0.6 g/L (providing 0.4 g/L of $\text{P}_3\text{O}_{10}^{5-}$ ions)

phosphorous acid (H_3PO_3)

25 3.0 g/L (providing 2.9 g/L of PO_3^{3-} ions)

resin solids

2.0 g/L

pH = 3.5 (adjusted with sodium hydroxide)

The water soluble resin was the same as in Example 1.

30 Example 6

Tin-plated DI can was cleaned using the same conditions as in Example 1 and was then treated with a 15-second spray of surface-treatment liquid composition 6 heated to 60° C. This treatment was followed with a water rinse and
35 drying using the same conditions as in Example 1. This treated can was subjected to an evaluation of the corrosion resistance, adherence, and slideability, and the stability

of surface-treatment liquid composition 6 was also evaluated.

Surface-treatment liquid composition 6

- 75% phosphoric acid (H_3PO_4)
5 10.0 g/L (providing 7.2 g/L of PO_4^{3-} ions)
sodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$)
 1.0 g/L (providing 0.4 g/L of $\text{P}_2\text{O}_7^{4-}$ ions)
hypophosphorous acid (H_3PO_2)
 2.0 g/L (providing 1.9 g/L of PO_2^{3-} ions)
10 resin solids
 2.0 g/L of water soluble resin 2
pH = 4.0 (adjusted with sodium hydroxide)

Water soluble resin 2 was the same as water soluble resin 1, except that only one-quarter rather than one-half
15 of the X's and Y's in the general formula were Z groups. Water soluble resin 2 was synthesized as for water soluble resin 1 but with 60 g of poly-4-vinylphenol, 20 g of 2-methylaminoethanol, and 20 g of 37% formaldehyde solution.

Example 7

- 20 Tin-plated DI can was cleaned using the same conditions as in Example 1 and was then treated with a 30 second spray of surface treatment liquid composition 7 heated to 50° C. This treatment was followed with a water rinse and drying using the same conditions as in Example 1. This
25 treated can was subjected to an evaluation of the corrosion resistance, adherence, and slideability, and the stability of surface-treatment liquid composition 7 was also evaluated.

Surface-treatment liquid composition 7

- 30 75% phosphoric acid (H_3PO_4)
 10.0 g/L (providing 7.2 g/L of PO_4^{3-} ions)
sodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$)
 1.0 g/L (providing 0.4 g/L of $\text{P}_2\text{O}_7^{4-}$ ions)
phosphorous acid (H_3PO_3)
35 2.0 g/L (providing 1.9 g/L of PO_3^{3-} ions)
resin solids
 2.0 g/L of water soluble resin 3

pH = 6.0 (adjusted with sodium hydroxide)

Water soluble resin 3 had an average value for n in the general formula of 70, half of the X's and Y's in the general formula were Z, and Z was $-\text{CH}_2\text{N}(\text{CH}_3)_2$. Water soluble resin 3 was synthesized as for water soluble resin 1 but from 60 g of poly-4-vinylphenol, 23 g of dimethylamine, and 40 g of 37 % formaldehyde solution.

Example 8

Tin-plated DI can was cleaned using the same conditions as in Example 1 and was then treated with a 30 second spray of surface treatment liquid composition 8 heated to 40° C. This treatment was followed with a water rinse and drying using the same conditions as in Example 1. This treated can was subjected to an evaluation of the corrosion resistance, adherence, and slideability, and the stability of surface treatment liquid composition 8 was also evaluated.

Surface-treatment liquid composition 8

75% phosphoric acid (H_3PO_4)
10.0 g/L (providing 7.2 g/L of PO_4^{3-} ions)
sodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$)
1.0 g/L (providing 0.4 g/L of $\text{P}_2\text{O}_7^{4-}$ ions)
hypophosphorous acid (H_3PO_2)
2.0 g/L (providing 1.9 g/L of PO_2^{3-} ions)
resin solids
0.4 g/L of water soluble resin 4
pH = 5.0 (adjusted with sodium carbonate)

Water soluble resin 4 was the same as water soluble resin 1, except that the average value of n in the general formula was only 3. Water soluble resin 4 was synthesized as for water soluble resin 1, but from 60 g of poly 4-vinylphenol with an average molecular weight of 360, 40 g of 2-methylaminoethanol, and 40 g of 37 % formaldehyde solution.

Comparison Example 1

Tin-plated DI can was cleaned using the same conditions as in Example 1 and was then treated with a 30 second

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spray of surface-treatment liquid composition 9 heated to 60° C. This treatment was followed with a water rinse and drying using the same conditions as in Example 1. This treated can was subjected to an evaluation of the corrosion resistance, adherence, and slideability, and the stability of surface-treatment liquid composition 9 was also evaluated.

Surface-treatment liquid composition 9

75% phosphoric acid (H_3PO_4)
10 10.0 g/L (providing 7.2 g/L of PO_4^{3-} ions)
sodium pyrophosphate ($Na_4P_2O_7 \cdot 10H_2O$)
1.0 g/L (providing 0.4 g/L of $P_2O_7^{4-}$ ions)
resin solids
0.4 g/L of water soluble resin 1 as in Example 1.
15 pH = 5.0 (adjusted with sodium carbonate)

Comparison Example 2

Tin-plated DI can was cleaned using the same conditions as in Example 1 and was then treated with a 30 second spray of surface treatment liquid composition 10 heated to 60° C. This treatment was followed with a water rinse and drying using the same conditions as in Example 1. This treated can was subjected to an evaluation of the corrosion resistance, adherence, and slideability, and the stability of surface-treatment liquid composition 10 was also evaluated.

Surface-treatment liquid composition 10

75% phosphoric acid (H_3PO_4)
20.0 g/L (providing 14.4 g/L of PO_4^{3-} ions)
sodium pyrophosphate ($Na_4P_2O_7 \cdot 10H_2O$)
30 1.0 g/L (providing 0.4 g/L of $P_2O_7^{4-}$ ions)
phosphorous acid (H_3PO_3)
0.1 g/L (providing 0.095 g/L of PO_3^{3-} ions)
resin solids
8.0 g/L of water soluble resin 1 as in Example 1
35 pH = 4.0 (adjusted with sodium hydroxide)

Comparison Example 3

5 Tin-plated DI can was cleaned using the same conditions as in Example 1 and was then treated with a 30 second spray of surface treatment liquid composition 11 heated to 60° C. This treatment was followed with a water rinse and drying using the same conditions as in Example 1. This treated can was subjected to an evaluation of the corrosion resistance, adherence, and slideability, and the stability of surface-treatment liquid composition 11 was also evaluated.

Surface-treatment liquid composition 11

75% phosphoric acid (H_3PO_4)
10.0 g/L (providing 7.2 g/L of PO_4^{3-} ions)
resin solids
15 2.0 g/L of water soluble resin 1 as in Example 1
pH = 4.0 (adjusted with sodium carbonate)

Comparison Example 4

20 Tin-plated DI can was cleaned using the same conditions as in Example 1 and was then treated with a 30 second spray of surface treatment liquid composition 12 heated to 60° C. This treatment was followed with a water rinse and drying using the same conditions as in Example 1. This treated can was subjected to an evaluation of the corrosion resistance, adherence, and slideability, and the stability of surface treatment liquid composition 12 was also evaluated.

Surface-treatment liquid composition 12

75% phosphoric acid (H_3PO_4)
1.0 g/L (providing 0.72 g/L of PO_4^{3-} ions)
30 resin solids
2.0 g/L of water soluble resin 1 as in Example 1
pH = 7.0 (adjusted with sodium hydroxide)

Comparison Example 5

35 Tin-plated DI can was cleaned using the same conditions as in Example 1 and was then treated with a 30 second spray of surface treatment liquid composition 13 heated to 60° C. This treatment was followed with a water rinse and

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drying using the same conditions as in Example 1. This
treated can was subjected to an evaluation of the corrosion
resistance, adherence, and slideability, and the stability
of surface-treatment liquid composition 13 was also evalu-
ated.

5 Surface-treatment liquid composition 13

75% phosphoric acid (H_3PO_4)

10.0 g/L (providing 7.2 g/L of PO_4^{3-} ions)

sodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$)

10 1.0 g/L (providing 0.4 g/L of $\text{P}_2\text{O}_7^{4-}$ ions)

resin solids

0.05 g/L of water soluble resin 1 as in Example
1

pH = 4.0 (adjusted with sodium carbonate)

15 Comparison Example 6

Tin-plated DI can was cleaned using the same condi-
tions as in Example 1 and was then treated with a 30 second
spray of surface treatment liquid composition 14 heated to
60° C. This treatment was followed with a water rinse and
20 drying using the same conditions as in Example 1. This
treated can was subjected to an evaluation of the corrosion
resistance, adherence, and slideability, and the stability
of surface treatment liquid composition 14 was also evalu-
ated.

25 Surface-treatment liquid composition 14

75% phosphoric acid (H_3PO_4)

1.0 g/L (providing 0.72 g/L of PO_4^{3-} ions)

sodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$)

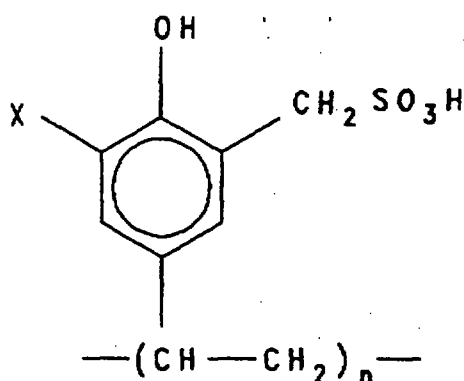
1.0 g/L (providing 0.4 g.L of $\text{P}_2\text{O}_7^{4-}$ ions)

30 resin solids

2.0 g/L of water soluble resin 5

pH = 4.0 (adjusted with sodium hydroxide)

Water-soluble resin 4 had the chemical formula:



The average value of n was about 40.

15 Water-soluble resin 4 was synthesized as follows: 50 g of poly{4-vinylphenol} (molecular weight = about 5,000) was placed in a 1,000 mL reaction flask equipped with a condenser, nitrogen inlet tube, overhead stirrer, and thermometer, and 500 g of 1,4-dioxane was added for dissolution.

20 An amount of 80 g of liquid sulfur trioxide (SO_3) was added over a time of 1 hour while the mixture was maintained at around 10°C . This was followed by heating to 80°C and reaction for 4 hours while stirring. Neutralization was carried out with 10 % sodium hydroxide solution

25 and the solvent was distilled off.

The various results are reported in Table 1, and they confirm that the surface treatment liquid compositions according to the present invention have excellent stability and also forms a film having an excellent corrosion resistance, adherence, and slideability.

30

Table 1: TEST RESULTS

		<u>IEV</u>	<u>Peel Strength, kgf/5 mm-width</u>	<u>Friction Coefficient</u>	<u>Stability</u>
5	Example 1	40	2.0	0.8	+
	Example 2	40	2.0	0.8	+
	Example 3	50	2.0	0.8	+
	Example 4	40	2.0	0.8	+
	Example 5	40	2.0	0.8	+
10	Example 6	60	2.0	0.8	+
	Example 7	40	2.0	0.8	+
	Example 8	60	2.0	0.8	+
	Comparison Example 1	40	2.0	0.8	x
15	Comparison Example 2	50	2.0	0.8	x
	Comparison Example 3	250	1.5	1.0	x
	Comparison Example 4	950	1.3	1.0	x
20	Comparison Example 5	500	1.5	1.0	x
	Comparison Example 6	750	1.3	1.0	x

25

Notes for Table 1

+ = no precipitation

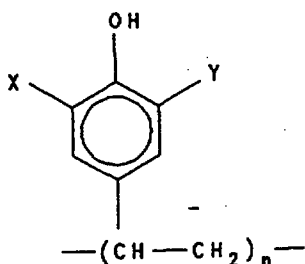
x = precipitation



CLAIMS

1. An aqueous liquid composition for treating the surface of tin-plated DI cans, having a pH in the range of from 2.0 to 6.5, and which besides water comprises the following components:

- (A) from 1 to 30 grams per litre of phosphate ions,
- (B) from 0.1 to 5 grams per litre of condensed phosphate ions,
- (C) from 0.5 to 5 grams per litre of reducing agent, and
- (D) from 0.1 to 20 grams (of dissolved solids) per litre of one or more water-soluble resin(s) being a polymer substantially consisting of monomeric units conforming to the general formula:

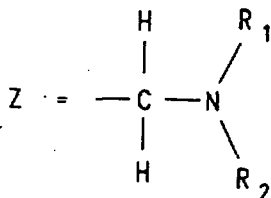


(I)

wherein:

n is an integer with a value in the range of from 2 to 80 for individual monomeric units in the resin but may have a non-integral average value for the resin component as a whole;

X and Y, independently of each other and independently for each monomeric unit, each represents either an hydrogen atom or a group "Z" with the following general formula:



(II)

(in which R_1 and R_2 , independently of each other and independently for each Z group in the monomeric unit,

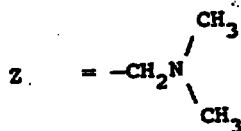


each represents a C_1 to C_{10} alkyl and/or hydroxyalkyl moiety);

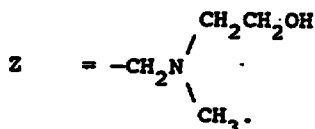
provided that the total number of Z groups present in the resin component is in the range of from 30 to 200 % of the total number of aromatic rings in the resin component.

2. A liquid composition according to claim 1, which substantially consists only of water and the specified components (A)-(D).

3. A liquid composition according to claim 1 or claim 2, wherein the groups Z in the general formula I have one of the following formulae:



and



4. A liquid composition according to any of the preceding claims, wherein the source of the phosphate ion component (A) is phosphoric acid and/or sodium phosphate.

5. A liquid composition according to any of the preceding claims wherein the concentration of the phosphate ion component (A) is in the range of from 5 to 15 grams per litre.

6. A liquid composition according to any of the preceding claims, wherein the condensed phosphate ions are one or a mixture of more than one of the following, namely pyrophosphate, tripolyphosphate and/or tetrapolyphosphate ions.

7. A liquid composition according to any of the preceding claims, wherein the concentration of the condensed phosphate ions is in the range of from 0.4 to 1 gram per litre.



8. A liquid composition according to any of the preceding claims, wherein the reducing agent component is one or a mixture of more than one of the following, namely phosphorous acid, hypophosphorous acid and/or salts of said acids.
 9. A liquid composition according to any of the preceding claims, wherein the concentration of the reducing agent component (C) is in the range of from 1 to 3 grams per litre.
 10. A liquid composition according to any of the preceding claims and substantially as herein described in or with reference to any of the Examples.
 11. A process for treating a tin-plated steel surface, in which said surface is contacted, for a period of from 2 to 60 seconds, with a composition according to any of the preceding claims at a temperature in the range from 22 to 80°C.
 12. A process according to claim 11, in which the temperature employed is in the range of from 40 to 60°C.
 13. A process according to claim 11 or claim 12 and substantially as herein described in or with reference to any of the Examples.
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