



Europäisches Patentamt

(19)

European Patent Office

Office européen des brevets

(11) Publication number:

0 043 680
A1

(12)

EUROPEAN PATENT APPLICATION

(21) Application number: **81302888.3**

(51) Int. Cl.³: **C 23 G 1/20, C 23 G 1/18**

(22) Date of filing: **26.06.81**

(30) Priority: **27.06.80 US 163566**

(71) Applicant: **AMCHEM PRODUCTS, INC., Brookside Avenue, Ambler Pennsylvania 19002 (US)**

(43) Date of publication of application: **13.01.82**
Bulletin 82/2

(72) Inventor: **McCready, Newton Willoughby, 54 Liangollen Lane, Newton Square Pennsylvania 19073 (US)**

(84) Designated Contracting States: **BE DE FR GB IT NL SE**

(74) Representative: **Sanderson, Laurence Andrew et al, Sanderson & Co. European Patent Attorneys 97 High Street, Colchester Essex (GB)**

(54) **Aqueous, alkaline cleaning solution and process for removing contaminants from a tin surface, as well as solid cleaning composition and cleaning concentrate for use therein.**

(57) An aqueous alkaline cleaning solution for removing lubricants or other soiling contaminants from tin without visibly etching it has a pH of about 11 to 13, imparted by an effective amount of an alkaline component and also contains, serving as inhibitor, from 0.02 g/l to 0.06 g/l of one or more quinones and/or polyhydroxybenzenes, these being either unsubstituted or substituted with halo, alkyl, alkoxy, carboxyl, nitro and/or cyano substituents. To prevent precipitation of the calcium and/or magnesium ions which cause water-hardness the solutions desirably contain at least about 0.1 g/l of a polyelectrolyte. The cleaning process using these solutions is operated at from about 100°F to about 130°F (approx. 38°C to 54°C). A solid cleaning composition or an aqueous concentrate can be dissolved in water to form the desired solution.

EP 0 043 680 A1

- 1 -

"AQUEOUS ALKALINE CLEANING SOLUTION AND
PROCESS FOR REMOVING CONTAMINANTS FROM A TIN
SURFACE, AS WELL AS SOLID CLEANING COMPOSITION
AND CLEANING CONCENTRATE FOR USE THEREIN."

This invention relates to an aqueous
alkaline cleaning solution and a process
employing that solution for cleaning tin
surfaces, as well as a solid cleaning composi-
5 tion and a cleaning concentrate for use in the
process.

This invention is particularly concerned
to provide a corrosion inhibitor for use in
the aqueous alkaline cleaning solution which
10 will deter or inhibit etching of the tin surface.
Although the invention is applicable to the
removal of contaminants from all kinds of tin
surface, it will here be described in connec-
tion primarily with the cleaning of tin-plated
15 surfaces, such as tin cans, which have been
soiled with organic lubricants of the kind
that are applied to the tin surface as drawing
aids during cold-forming operations.

Cleaning is an essential preliminary to
20 many surface-finishing operations. It is for
example normally necessary to clean any metal
surface prior to corrosion-preventive treat-
ments, and prior to the application of organic
finishes to the surface; and cleaning is
25 especially important in the case of metal
surfaces to which organic materials have been

recently applied as an aid to cold-forming. Such organic lubricating materials must be removed in order to make the metal surface suitably receptive to an organic or inorganic finish.

5

A typical and important example of a situation where preliminary cleaning is needed can be found in the manufacture of two-piece, tin-plated, so-called "drawn-and-ironed" cans.

10

Circular blanks of tin-plated steel (which, due to the high cost of tin, generally have only a thin layer of tin plating) are first cupped and then passed through several drawing dies, so as thus to "iron" the cup - in order thus

15

to form a unitary side-wall and can-bottom structure. Any can produced by this process will normally have a fairly characteristic shape, i.e. it will be a thin-walled, thick-bottomed container having a generally uniform

20

wall thickness; and such cans will be referred to herein as "DI" (drawn-and-ironed) cans.

25

The forming operations carried out during the manufacture of DI cans are normally assisted, and indeed the dies and the metallic surface are protected, by the application of lubricants to the tin-plate surface prior to or during the forming operation. The lubricants which are thus applied to the tin surface usually consist of various types of mineral and

30

vegetable oils and heavy metal soaps; and they must be removed if it is desired to have a clean surface in order to assure adhesion of a subsequently applied sanitary lacquer and/or decorative varnish.

35

One problem with DI tin-plated containers,

- 3 -

which can be serious, is that the drawing operation stretches the tin-plate surface, thereby exposing some of the underlying metal.

5 The underlying metal may very probably be a ferrous metal, such as iron or one of many iron alloys or of a wide variety of steels; and its exposure may easily lead to corrosion.

10 An effective cleaner for tin-plate is one which indeed will provide a water-break-free surface on the tin (a water-break-free surface is one which is sufficiently freed from lubricants, soil, and other contaminants so that it will maintain a continuous film of water) but which will do so without unduly 15 etching the tin and without promoting corrosion of the underlying metal.

Etching of the tin surface results from chemical attack of the cleaning solution thereon and results in a roughened and dull surface.

20 Inevitably etching also removes some of the corrosion-protective layer of tin from the underlying metal surface, thereby diminishing the anti-corrosion qualities of the tinned surface, and aggravating any corrosion 25 problems arising from exposure of the underlying metal. In the case of say a beverage can, where a smooth, shiny appearance is wanted and maximum safety of the contents is necessary, it is clear that etching and/or corrosion will 30 be highly undesirable.

Etching and corrosion can be an especially severe problem with conventional cleaners for tin-plate when during the cleaning operation line-stoppage can expose some of the cleaned 35 cans to the cleaner for excessive periods,

which can lead to etching and corrosion of the underlying metal surface (no matter whether exposed by stretching or by etching) so severe as to render the cans quite 5 unacceptable for use. Apart from appearance, any corrosion and blemishes on the surface will adversely affect the adhesion of any chemical conversion coating or sanitary lacquer coating that may thereafter be applied 10 to it.

The cleaners which have been found to be most suitable for producing the desired water-break-free surface on the tin are alkaline cleaners, such as aqueous solutions of alkali 15 metal salts of silicates, phosphates, carbonates and borates- but these all have the undesirable tendency to etch the surface. Efforts have therefore already been made to discover additives which will help to inhibit etching 20 of the tin surface under the alkaline conditions employed.

Broadly-speaking it is a fair generalization to say that the inhibited alkaline cleaning solutions hitherto suggested have mostly 25 required the use of long periods (for instance up to 15 minutes) and/or relatively high temperatures (at least 140°F [60°C] and often above 150°F [about 65°C]) to achieve satisfactory cleaning. In many instances the suggested 30 inhibitors give rise to waste-disposal and other problems arising from their toxicity or other characteristics.

United States Patent No. 4,094,701 discloses a process for cleaning a tin surface,

without substantially etching it, using an aqueous alkaline solution containing an alkaline component as well as one or more surfactants and, serving as inhibitor, an 5 organic tannin. This solution is sprayed on to the object to be cleaned at elevated temperature for about one to about two minutes. The pH of the cleaner is at least 9, and because higher pH values tend gradually 10 to inactivate the tannin it is preferably between 10 and 13, and most preferably between 10 and 10.5. When in the preferred pH range of say from 9 to 10.5 this cleaner is to be employed at temperatures of 140°F (60°C) and 15 upwards. Thus, while it is true that this United States Patent No. 4,094,701 does disclose a cleaning solution that can be used for cleaning tin surfaces, without etching, at temperatures below boiling in periods of 20 less than two minutes, nevertheless the use of temperatures in excess of 140°F (60°C) is still economically disadvantageous. Moreover the recommended alkaline components include alkali metal borates and phosphates, both of 25 which may give rise to environmental problems and, hence, plant-effluent treatment problems. There is thus today still an unfulfilled need for an effective economic and ecologically-acceptable cleaning solution and process which 30 may be used upon tin articles operating at temperatures lower than those previously found to be effective so as to produce a water-break-free surface thereon without etching the tin, no matter whether applied for the necessary

minimum periods of about one minute or less or whether by line-stoppage or other accident applied for much longer periods of time than had been intended - without the use of

5 components currently-regarded as environment-ally objectionable.

We have now found that this need can be largely or even wholly fulfilled by means of the cleaning solutions and processes herein-10 after described.

According to one aspect of this invention there are provided aqueous alkaline cleaning solutions for cleaning lubricants or other soiling contaminants from a tin surface 15 without visibly etching it, these solutions having a pH in the range of from about 11 to about 13 and containing effective amounts of an alkaline component and of an inhibitor which inhibitor is or includes one or more substituted 20 or unsubstituted quinones and/or substituted or unsubstituted polyhydroxy-benzenes.

The term "tin" as used herein refers not merely to pure tin metal but also to alloys wherein tin predominates; and the term "tin 25 surface" refers to the surface of not only articles made of tin but also those plated with tin.

It will of course be understood that by an "effective amount" of the alkaline component 30 we mean such a concentration as will substantially remove the lubricants or other soiling contaminants, leaving a water-break-free tin surface. Similarly by an "effective amount" of the inhibitor we mean such a concentration as is

- 7 -

able substantially to inhibit etching of the tin surface.

The term "polyhydroxy-benzenes" is here used to designate otherwise substituted or unsubstituted benzenes which bear at least two hydroxy substituents, in ortho-, meta- or para- positions, and perhaps more than two such hydroxy substituents arranged either symmetrically or asymmetrically.

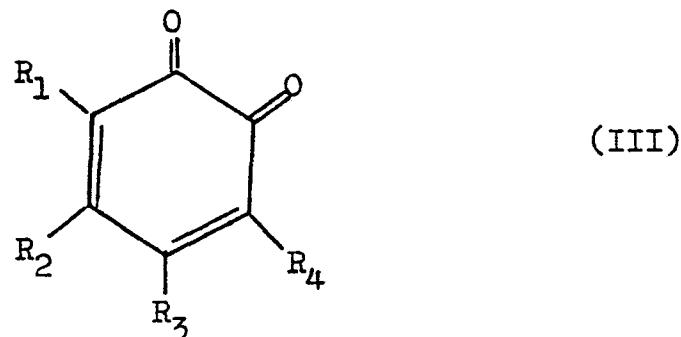
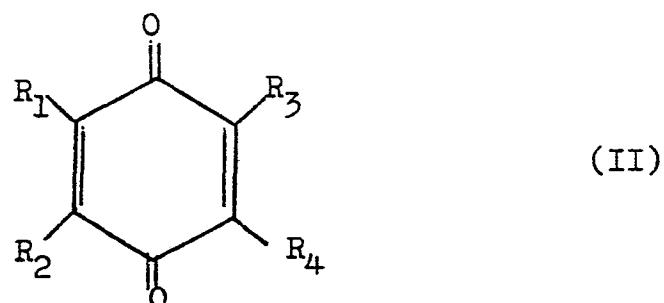
According to another aspect of this invention there is also provided a process for cleaning lubricants or other soiling contaminants from a tin surface without visibly etching it, in which the surface is brought into contact for a sufficient time at the chosen temperature with an aqueous alkaline cleaning solution as herein disclosed having a pH in the range of from about 11 to about 13 and containing effective amounts of an alkaline component and of an inhibitor which is or includes one or more substituted or unsubstituted quinones and/or substituted or unsubstituted polyhydroxy-benzenes.

The inhibitor used in the cleaning solution and process of this invention must be one or more substituted or unsubstituted quinones and/or substituted or unsubstituted polyhydroxy-benzenes. While the nature of the substituents (leaving aside the hydroxy substituents on the polyhydroxy-benzenes) does not seem to be of any fundamental significance, it can be noted for general guidance that such substituents, both upon the polyhydroxy-benzenes and the quinones, can include halo, alkyl,

carboxy, nitro, cyano and alkoxy substituents.

Exemplary quinones and substituted quinones useful as inhibitors in this invention include the substituted and unsubstituted

5 quinones according to general formulae II and III below:



wherein:

10 R_3 and R_4 , which may be the same or different, each represents a hydrogen atom or an alkyl, alkoxy, hydroxy, halo, nitro, cyano or carboxyl group; and

15 either R_1 and R_2 , which may be the same or different, each represents an atom or group defined in the same manner as for R_3 and R_4 or together R_1 and R_2 constitute an alkyldienyl group which in turn, together with the quinone ring to which they are attached, forms a napthaquinone.

Exemplary substituted or unsubstituted polyhydroxy-benzene inhibitors, of particular interest for use in this invention, include for instance catechol (ortho-dihydroxy benzene) and/or resorcinol (meta-dihydroxy benzene) and/or hydroquinone (1,4-dihydro-benzoquinone or para-dihydroxy benzene) and/or hydroxy-hydroquinone (1,2,4-trihydroxybenzene and/or 1,3,5-trihydroxybenzene and/or gallic acid (3,4,5-trihydroxybenzoic acid and/or 1,2,4,5-tetrahydroxybenzene.

Preferred inhibitors for use in this invention include gallic acid (3,4,5-trihydroxybenzoic acid), 1,2,3-benzene-triol and dihydroxybenzenes as well as quinones, such as 1,4-benzenediol and 1,4-benzoquinone.

The inhibitor must naturally be added in an amount effective to inhibit etching of the tin surface. Generally, the necessary minimum concentration of the inhibitor will increase with the concentration of the alkaline component. Moreover, since "soft" water tends to be more corrosive than "hard" water (as will be further discussed below) generally the necessary minimum concentration of inhibitor will tend to be greater when the cleaning solutions are made-up with soft water than when they are made-up with hard water. The concentration of inhibitor in the solution will advantageously be at least about 0.02 g/l; and it will preferably be in the range of from about 0.02 g/l to about 0.06 g/l. There is no objection to the use of concentrations greater than 0.06 g/l, but generally the resultant increase in cost is

not repaid by a greater inhibition of etching.

The addition of a polyelectrolyte to the cleaning solutions of the invention has been found to be beneficial since then the solution 5 may be employed effectively irrespective of the hardness of the water used to make-up the solution.

Hardness is a characteristic of water, generally accepted to represent the total 10 concentration of calcium and magnesium ions - although other polyvalent cations, seldom present in more than trace amounts, may sometimes also contribute to hardness. The determination of hardness can be carried out by 15 titration, as described in "Standard Methods of Test for Hardness in Water", Designation D 1126-67 (Reapproved 1974) published by the American Society for Testing Materials.

Hardness may conveniently be expressed in parts 20 per million (ppm) of calcium carbonate equivalent; the higher the value, the greater being the hardness. Usually water having a hardness of less than about 100 ppm will be regarded as "soft", whereas with a hardness about about 25 100 ppm it will be regarded as "hard". Water-hardness can vary greatly from place to place. In some coastal regions of the United States the hardness may be only about 50 ppm to about 30 100 ppm, but it may increase to about 300 ppm where the water runs somewhere through limestone deposits, and in some areas of the Midwest of the United States the hardness may be as much as from about 400 ppm to about 35 500 ppm.

- 11 -

When the water used to make-up the alkaline aqueous solutions of this invention is rather hard then, unless indeed polyelectrolytes are present, there is a tendency to experience precipitation of the calcium and magnesium ions that cause water hardness. The greater the hardness of the water the greater usually will be the degree of precipitation. Any such precipitation is potentially a problem, since it may result in sediment which is liable, for example, to clog spray nozzles when spraying is the chosen method of application. The use of softer water is moreover not an altogether satisfactory answer to this problem. As hardness decreases, the water may tend to become more corrosive. A polyelectrolyte is therefore a very desirable, though optional, component of the cleaning solutions of this invention.

Polyelectrolytes are high molecular weight electrolytes; and they are either of natural origin, such as proteins, or they are of a synthetic nature, such as polymerized organic acids. Since the polyelectrolytes in solution do not dissociate to give a uniform distribution of positive and negative ions, as do simple electrolytes, the ions of one sign are bound to the polymer chain. Thus, for instance, the negative charges may be in the polymer chain, and only positive ions will be free to diffuse through the solvent.

The polyelectrolytes used in the solutions of this invention can be any of the compounds known to prevent precipitation of the minerals

which cause water-hardness, but certain preferences can usefully be borne in mind. Because phosphates may be regarded as environmentally-objectionable, we prefer

5 to use a polyelectrolyte which does not contain phosphates, since then the plant effluent will not contain phosphates. We also prefer to avoid the use of the previously-employed alkali metal tripolyphosphates,

10 because these may have the deleterious effect of promoting etching or de-tinning. Because they do not promote de-tinning and possibly may to some extent inhibit etching the polyelectrolytes which we prefer for use in the

15 cleaning solutions of the present invention are polyelectrolytes such as Gantrez S-95, manufactured by GAF Corporation, and Tamol 960 manufactured by Rohm and Haas Company.

The polyelectrolytes will preferably be

20 present in a concentration which is effective substantially to prevent precipitation of the calcium and magnesium ions that are the primary cause of water-hardness. Generally, the greater the hardness of the water the greater will be

25 the desired concentration of the polyelectrolyte. We have found that the concentration of polyelectrolyte will preferably be at least about 0.1 g/l, and most advantageously in the range of from about 0.1 g/l to about 1 g/l. There

30 is no objection to the use of concentrations in excess of 1 g/l, but in our experience such higher concentrations do not result in any significant improvement.

One or more surfactants or wetting agents

can usefully be added to the aqueous alkaline cleaning solutions of the present invention, so as to enhance the performance of the cleaning solution in a conventional manner - 5 but the presence or absence of surfactants has no noticeable effect as regards either inhibiting or promoting the etching of the tin surface by the cleaning solution.

Supposing a surfactant is added which is not 10 a low-foaming surfactant, then a defoaming agent will also desirably be added - since otherwise foaming can become so serious as to cause delay or even shut-down in a commercial cleaning line.

15 The surfactants and wetting agents employed in the cleaning solutions can for instance be ethoxylated straight-chain alcohols and octyl or nonyl phenoxy polyethoxyethanol. Non-ionic surfactants are usually preferred since 20 they are low-foaming.

The cleaning solutions will preferably contain at least about 0.2 g/l of the surfactant(s); particularly preferred concentrations are in the range of from about 0.2 g/l to 25 about 0.5 g/l.

As already indicated, the cleaning solution must have a pH value (determined at a solution temperature of about 27°C) within the range of from about 11 to about 13; and 30 will preferably have a pH value within the range of from about 12 to about 12.8.

The alkaline component used in the cleaning solution and process of this invention may be of any kind known to produce an alkaline

solution when dissolved in water; but it will preferably not be an environmentally-object-ionable one. The alkaline component therefore can advantageously be one or a mixture of more than one alkali metal hydroxides and/or carbonates and/or silicates and/or ammonium hydroxides and/or carbonates. A particularly preferred alkaline component is a mixture of sodium carbonate, sodium metasilicate and either sodium hydroxide or potassium hydroxide or both.

The alkaline component must naturally be present in a concentration which will be effective substantially to remove lubricants or other such soiling contaminants. The minimum effective amount may be readily determined in the conventional manner. The concentration of alkaline component in the solution will preferably be at least about 2 g/l, and more advantageously will be in the range of from about 3g/l to about 5 g/l. Greater concentrations may be employed, but the benefit to be gained thereby is generally not significant.

Tin surfaces may be cleaned by contacting them with the aqueous alkaline cleaning solutions of the present invention for a sufficient time at the chosen temperature to remove lubricants or other such soiling contaminants therefrom, without visibly etching the tin surface. Usually the solution temperature should be at least about 100°F (38°C); and it will preferably be in the range of from about 100°F to about 130°F (38° to 54°C) and above all from about 115°F to about 125°F (46° to 52°C). The optimum temperature may tend to be somewhat higher for solutions with low

concentrations of alkaline components than for solutions with higher concentrations thereof - or, put another way, the optimum treatment temperature tends somewhat to vary inversely with the pH of the cleaning solution.

5 The necessary period of treatment will generally depend on the method of application. Spraying is the preferred method, and when used the treatment time will tend to decrease as the spraying pressure increases. Operating at currently conventional spraying pressures
10 of about 25 psig (pounds per square inch, guage pressure) to about 35 psig (1.76 to 2.46 kg/cm²) it should be found that treatment times of from about 40 seconds up to about one minute may be sufficient to produce a water-break-free surface. If one employs the already-
15 known but little used spraying pressures of 60 psig to 100 psig (4.22 to 7.03 kg/cm²) then the treatment times may be reduced, perhaps to as little as from about 1 to 5 seconds.

20 The treatment time may need to be increased the longer the interval between manufacture of the tin-plated metal article and the cleaning thereof. With drawn-and-ironed tin-plated steel cans, an interval between manufacture and cleaning of as little as fifteen minutes may necessitate a noticeably increased cleaning
25 time. The necessary treatment time may also vary depending on the type of lubricant used in the manufacturing process; some being more readily removed than others.

30 In order to discover the extent to which the cleaning solutions of this invention will inhibit etching we have used treatment times of

up to about 30 minutes without visibly etching the tin; but in actual practice it is of course recommended to use the shortest treatment time which is effective to produce a 5 water-break-free surface without etching the tin.

After the tin surface has been cleaned with the cleaning solution, the clean surface will generally be rinsed at least once with tap 10 water, and then may advantageously be rinsed with deionized water and dried at an elevated temperature, preferably one in the range of from about 350° to about 400°F (177° to 205°C).

It is convenient to make up the cleaning 15 solutions of the present invention from either an aqueous concentrate or a solid cleaning composition, which can simply be added to water to produce the desired aqueous alkaline cleaning solutions.

Such an aqueous concentrate may 20 advantageously be formulated so that when added to water at a concentration in the range of from about 0.5% to about 2% by volume, and preferably in the range of from about 1% to 25 about 2% by volume, it produces an aqueous alkaline cleaning solution having a pH of about 11 to about 13, and comprises an alkaline component in an amount effective substantially to remove contaminants from the tin surface, 30 as well as one of the herein-defined inhibitors in an amount effective to inhibit etching of the surface. The alkaline component will preferably constitute up to about 770 grams per litre, and advantageously from about 250 to 35 about 500 grams per litre of the concentrate.

The inhibitor will preferably constitute at least about 2 grams per litre, and advantageously from about 2 to about 6 grams per litre of the concentrate. The concentrate optionally but desirably will also contain polyelectrolyte(s) and/or surfactant(s). The polyelectrolyte will desirably be present in a concentration within the range of from about 10 to about 20 grams per litre.

Alternatively a solid cleaning composition may advantageously be formulated so that when added to water at a concentration of from about 3 g/l to about 7 g/l, and preferably from about 4.6 g/l to 6.7 g/l, it will produce an aqueous alkaline cleaning solution having a pH of about 11 to about 13 and contains an effective amount of an alkaline component and an effective amount of an inhibitor as defined above. The alkaline component will preferably constitute at least about 15% by weight of the composition.

The inhibitor will preferably constitute at least about 0.1% by weight, and most advantageously from about 0.5% to about 2% by weight of the composition. Moreover the composition optionally but desirably will also contain a polyelectrolyte, present preferably in a concentration of up to about 10% by weight, and most advantageously in a concentration of from about 3% to about 10% by weight of the composition.

The balance (if any) of the cleaning composition may consist of diluents and the like, that is to say compounds which can be regarded as inert with respect to any possible influence, either positive or negative, upon the cleaning and non-etching properties of the cleaning solutions of the invention. A typical but merely illustrative example of such compounds is for

instance sodium sulphate.

In order that the invention may be well understood, it will now be described in more detail, but only by way of illustration, in the following examples:

EXAMPLES

It should first be noted that, in each of the 5 following Examples, sets of "drawn-and-ironed" tin-plated steel cans (previously defined and hereinafter called DI cans) were contacted with the specified cleaning solution within 24 hours of their manufacture, and without any other treatment prior to contact with the cleaning solutions 10 of the invention.

The cleaning solutions were made up from solid cleaning compositions having the components indicated in Table I below present in the percentages there shown. Each such composition is identified in Table I and elsewhere 15 by a number and the subscript "c". The solutions were made up by dissolving a specific amount, in grams, of each composition as indicated in Table II below to 6 litres of water, to form aqueous alkaline cleaning solutions having the concentrations of components (including surfactants) 20 indicated in Table III below. Each such cleaning solution is identified in Table III and elsewhere by the number of the composition from which it has been made, coupled with the subscript "s".

In each of the Examples the sets of cans were contacted 25 with the cleaning solution by spraying them with the solutions at about 25psi (1.76 kg/cm²) for the periods and at the temperatures there stated; and afterwards the cans were then rinsed with water, and visually examined for etching and appearance.

TABLE I

COMPONENTS	SOLID COMPOSITIONS (Percentages by weight)					
	1c	2c	3c	4c	5c	6c
<u>Inhibitors</u>						
3,4,5-trihydroxybenzoic acid	0.83	1.26	1.93	X	1.24	1
1,2,3-benzenetriol	X	X	X	X	X	X
1,4-benzenediol	X	X	X	X	X	X
1,4-benzoquinone	X	X	X	X	X	X
<u>Alkaline Compounds</u>						
NaOH	39.67	39.5	39.23	40	98.76	64
Na ₂ CO ₃	54.56	54.33	53.95	55	X	30
Na ₂ SiO ₃	X	X	X	X	X	X
<u>Polyelectrolytes</u>						
Gantrez S-95	4.94	4.91	4.89	5	X	5
Sodium tripolyphosphate	X	X	X	X	X	X

continued :

Note re Table I above:

Gantrez S-95 is a polyelectrolyte manufactured by
GAF Corporation.

TABLE I (continued)

COMPONENTS	SOLID COMPOSITIONS (Percentages by weight)					
	7c	8c	9c	10c	11c	12c
<u>Inhibitors</u>						
3,4,5-trihydroxybenzoic acid	1	1	0.9	X	X	X
1,2,3-benzenetriol	X	X	X	9.83	X	X
1,4-benzenediol	X	X	X	X	X	9.83
1,4-benzoquinone	X	X	X	X	9.83	X
<u>Alkaline Compounds</u>						
NaOH	34	30	40	36.07	36.07	36.07
Na ₂ CO ₃	60	20	39.6	36.07	36.07	36.07
Na ₂ SiO ₃	X	44	15	X	X	X
<u>Polyelectrolytes</u>						
Gantrez S-95	.5	5	4.5	X	X	X
Sodium tripolyphosphate	X	X	X	18.03	18.03	18.03

0043680

- 21 -

TABLE II

Solid Composition No.	1c	2c	3c	4c	5c	6c
Grams of Composition per 6 litres of Water	27.73	27.85	28.04	27.5	31.6	39.94
Water Used*						
Deionized	+	+	+	+		
Tap Water**					+	+
Solid Composition No. (continued)	7c	8c	9c	10c	11c	12c
Grams of Composition per 6 litres of Water	40.05	40.09	27.45	30.5	30.5	30.5
Water Used*						
Deionized				+	+	+
Tap Water**	+	+	+			

Notes re Table II above :

* A "+" indicates the water used

** The tap water used was relatively hard having a hardness of about 300 ppm.

TABLE III

COMPONENTS	Aqueous Alkaline Cleaning Solution (concentrations in grams/litre)					
	1s	2s	3s	4s	5s	6s
<u>Inhibitors</u>						
3,4,5-trihydroxybenzoic acid	0.038	0.058	0.09	X	0.054	0.067
1,2,3-benzenetriol	X	X	X	X	X	X
1,4-benzenediol	X	X	X	X	X	X
1,4-benzoquinone	X	X	X	X	X	X
<u>Alkaline Compounds</u>						
NaOH	1.83	1.83	1.83	1.83	5.2	4.26
Na ₂ CO ₃	2.52	2.52	2.52	2.52	X	2
Na ₂ SiO ₃	X	X	X	X	X	X
<u>Polyelectrolytes</u>						
Gantrez S-95	0.23	0.23	0.23	0.23	X	0.33
Sodium tripoly-phosphate	X	X	X	X	X	X
<u>Surfactants</u>						
Poly-Tergent S-505-LF	X	X	X	X	X	0.67
Plurafac D-25	0.33	0.33	0.33	0.33	0.35	X
Plurafac A-38	X	X	X	X	X	X
Tergitol Min-Foam IX	X	X	X	X	X	X
<u>Defoamers</u>						
Pluronic 31R1	0.83	0.83	0.83	0.83	0.087	X
Solution pH	12.7	12.7	12.7	12.7	12.8	12.6

(continued)

TABLE III (continued)

COMPONENTS	Aqueous Alkaline Cleaning Solution (concentrations in grams/litre)					
	7s	8s	9s	10s	11s	12s
<u>Inhibitors</u>						
3,4,5-trihydroxybenzoic acid	0.067	0.067	0.041	X	X	X
1,2,3-benzenetriol	X	X	X	0.49	X	X
1,4-benzenediol	X	X	X	X	X	0.49
1,4-benzoquinone	X	X	X	X	0.49	X
<u>Alkaline Compounds</u>						
NaOH	2.27	2	1.83	1.83	1.83	1.83
Na ₂ CO ₃	4	1.33	1.82	1.83	1.83	1.83
Na ₂ SiO ₃	X	2.94	0.69	X	X	X
<u>Polyelectrolytes</u>						
Gantrez S-95	0.33	0.33	0.21	X	X	X
Sodium tripoly-phosphate	X	X	X	0.92	0.92	0.92
<u>Surfactants</u>						
Poly-Tergent S-505-LF	0.67	X	X	X	X	X
Plurafac D-25	X	0.35	0.33	X	X	X
Plurafac A-38	X	0.083	X	X	X	X
Tergitol Min-Foam IX	X	X	X	0.42	0.42	0.42
<u>Defoamers</u>						
Pluronic 31R1	X	0.23	0.083	X	X	X
Solution pH	12.3	12.3	12.6	12.4	12.4	12.4

Notes re Table III above :

- (a) Gantrez S-95 is a polyelectrolyte manufactured by GAF Corporation
- (b) Poly-Tergent S-505-LF is a surfactant manufactured by Olin Corporation
- (c) Plurafac D-25 is a surfactant manufactured by BASF Wyandotte Corporation
- (d) Plurafac A-38 is a surfactant manufactured by BASF Wyandotte Corporation
- (e) Tergiton Min-Foam IX is a surfactant manufactured by Union Carbide Corporation
- (f) Pluronic 31R1 is a defoamer manufactured by BASF Wyandotte Corporation
- (g) The solution pH was measured at a solution temperature of about 27°C.

Example 1

Sets of DI cans were sprayed, one set per solution, with cleaning solutions 1s, 2s, 3s and 4s, for 10 minutes at 123°F (about 51°C). The results obtained are summarized in Table IV as follows :

TABLE IV

<u>Cleaning Solution</u>	<u>Observation of Result</u>
1s	No de-tinning; water-break-free cans; bright, rust-free surface
2s	No de-tinning; water-break-free cans; bright, rust-free surface
3s	No de-tinning; water-break-free cans; bright, rust-free surface
4s	Severe de-tinning

Example 2

Sets of DI cans were sprayed, one set per test, with cleaning solution 5s for the times and at the temperatures indicated; and the results obtained are summarized in Table V as follows :

TABLE V

<u>Solution Temperature</u>	<u>Treatment Time</u>	<u>Observed Result</u>
125°F (\approx 52°C)	1 minute	No de-tinning; bright, rust-free surface; water-break-free cans
125°F (\approx 52°C)	30 minutes	No de-tinning; bright, rust-free surface; water-break-free cans
127°F (\approx 53°C)	1 minute	No de-tinning; bright, rust-free surface; water-break-free cans
127°F (\approx 53°C)	30 minutes	No de-tinning; bright, rust-free surface; water-break-free cans

Example 3

Sets of DI cans were sprayed with cleaning solutions 6s, 7s, 8s and 9s, one set per test, for the times and at the temperatures indicated. The results are summarized in Table VI.

TABLE VI

<u>Cleaning Solution</u>	<u>Solution Temperature</u>	<u>Treatment Time</u>	<u>Observed Result</u>
6s	120° F (~49° C)	1 minute	No de-tinning; bright, rust-free surface; water-break-free cans
7s	120° F (~49° C)	1 minute	No de-tinning; bright, rust-free surface; water-break-free cans
8s	120° F (~49° C)	1 minute	No de-tinning; bright, rust-free surface; water-break-free cans
9s	120° F (~49° C)	1 minute	No de-tinning; bright, rust-free surface; water-break-free cans
9s	120° F (~49° C)	15 minutes	No de-tinning; bright, rust-free surface; water-break-free cans
9s	120° F (~49° C)	30 minutes	No de-tinning; bright, rust-free surface; water-break-free cans
9s	124° F (~51° C)	1 minute	No de-tinning; bright, rust-free surface; water-break-free cans
9s	124° F (~51° C)	15 minutes	No de-tinning; bright, rust-free surface; water-break-free cans
9s	124° F (~51° C)	30 minutes	No de-tinning; bright, rust-free surface; water-break-free cans

Example 4

Sets of DI cans were sprayed with cleaning solutions 10s, 11s, and 12s, one set per test, for the times and at the temperatures indicated; and the results observed are summarized in Table VII as follows :

TABLE VII

<u>Cleaning Solution</u>	<u>Solution Temperature</u>	<u>Treatment Time</u>	<u>Observed Result</u>
10s	125° F (\approx 52° C)	1 minute	No de-tinning; bright, rust-free surface; water-break-free cans
11s	125° F (\approx 52° C)	1 minute	No de-tinning; bright, rust-free surface; water-break-free cans
12s	125° F (\approx 52° C)	1 minute	No de-tinning; bright, rust-free surface; water-break-free cans
10s	125° F (\approx 52° C)	30 minutes	No de-tinning; bright, rust-free surface; water-break-free cans
11s	125° F (\approx 52° C)	30 minutes	No de-tinning; bright, rust-free surface; water-break-free cans
12s	125° F (\approx 52° C)	30 minutes	No de-tinning; bright, rust-free surface; water-break-free cans
10s	150° F (\approx 66° C)	1 minute	No de-tinning; bright, rust-free surface; water-break-free cans
11s	150° F (\approx 66° C)	1 minute	No de-tinning; bright, rust-free surface; water-break-free cans
12s	150° F (\approx 66° C)	1 minute	No de-tinning; bright, rust-free surface; water-break-free cans
10s	150° F (\approx 66° C)	30 minutes	No de-tinning; bright, rust-free surface; water-break-free cans

TABLE VII (continued)

<u>Cleaning Solution</u>	<u>Solution Temperature</u>	<u>Treatment Time</u>	<u>Observed Result</u>
11s	150° F (\approx 66° C)	30 minutes	No de-tinning; bright, rust-free surface; water-break-free cans
12s	150° F (\approx 66° C)	30 minutes	No de-tinning; bright, rust-free surface; water-break-free cans

Example 5

Aqueous concentrates were prepared having the concentrations of components indicated in Table VIII. These concentrates are designated 13 aq and 14 aq.

Aqueous alkaline cleaning solutions 13s and 14s were formulated, respectively, by diluting 11.4 millilitres of aqueous concentrate 13 aq to 1 litre with tap water, and by diluting 10 millilitres of aqueous concentrate 14 aq to 1 litre with deionized water. Surfactants were added in the concentrations indicated. The cleaning solutions had the concentrations of components indicated in Table VIII, as follows :

TABLE VIII

COMPONENTS	AQUEOUS CONCENTRATE (concentrations in g/l)		CLEANING SOLUTION (concentrations in g/l)	
	13 aq	14 aq	13s	14s
<u>Alkaline Compounds</u>				
KOH	300	112.6	3.42	1.13
Potassium Silicate	X	159.16	X	1.59
Na ₂ CO ₃	160.9	202.7	1.83	2.03
Sodium Silicate	125.5	X	1.43	X

(continued)

TABLE VIII (continued)

COMPONENTS	AQUEOUS CONCENTRATE (concentrations in g/l)		CLEANING SOLUTION (concentrations in g/l)	
	13 aq	14 aq	13s	14s
<u>Inhibitors</u>				
3,4,5-trihydroxy- -benzoic acid	4.02	4.5	0.046	0.05
<u>Polyelectrolytes</u>				
Gantrez S-95	18.5	22.5	0.21	0.23
<u>Surfactants</u>				
Plurafac D-25	X	X	0.33	X
<u>Defoamers</u>				
Pluronic 31R1	X	X	0.083	X
pH value	X	X	12.4	12.4

Notes re Table VIII above :

- (a) The potassium silicate employed was one manufactured by PQ Corporation and sold under the name Kasil No. 6
- (b) The sodium silicate employed was one manufactured by PQ Corporation and sold under the name "N" sodium silicate
- (c) The Gantrez S-95 used is a polyelectrolyte manufactured by GAF Corporation
- (d) The Plurafac D-25 used is a surfactant manufactured by BASF Wyandotte Corporation
- (e) The Pluronic 31R1 used is a defoamer manufactured by BASF Wyandotte Corporation
- (f) The pH value was measured at about 27°C.

Sets of DI cans were sprayed with cleaning solutions 13s and 14s, one set per test, for the times and at the temperatures indicated; and the results obtained are summarized in Table IX as follows :

TABLE IX

<u>Cleaning Solution</u>	<u>Solution Temperature</u>	<u>Treatment Time</u>	<u>Observed Result</u>
13s	120° F (\approx 49° C)	1 minute	No de-tinning; bright, rust-free surface; water-break-free cans
14s	120° F (\approx 49° C)	1 minute	No de-tinning; bright, rust-free surface; water-break-free cans
13s	124° F (\approx 51° C)	30 minutes	No de-tinning; bright, rust-free surface; water-break-free cans
13s	128° F (\approx 53° C)	30 minutes	No de-tinning; bright, rust-free surface; water-break-free cans

Example 6

Cleaning solutions 15s, 16s and 17s were prepared using tap water, and having the concentrations of components indicated in Table X below, solution 17s does not contain an inhibitor, and thus (like cleaning solution 4s in Example 1) is presented only for purposes of comparison.

TABLE X

<u>COMPONENT</u>	<u>CLEANING SOLUTION (g/l)</u>		
	15s	16s	17s
<u>Inhibitor</u>			
1,4-dihydroxybenzene	0.05	0.05	X
<u>Alkaline Compound</u>			
Na ₂ SiO ₃	4.33	4.33	4.33
<u>Polyelectrolyte</u>			
Tamol 960	0.67	0.47	0.67
<u>Surfactant</u>			
Poly-Tergent S-505-LF	0.42	0.42	0.42
pH	12.4	12.4	12.4

Notes re Table X above :

- (a) Tamol 960 is a polyelectrolyte manufactured by Rohm & Haas Company
- (b) Poly-Tergent S-505-LF is a surfactant manufactured by Olin Corporation

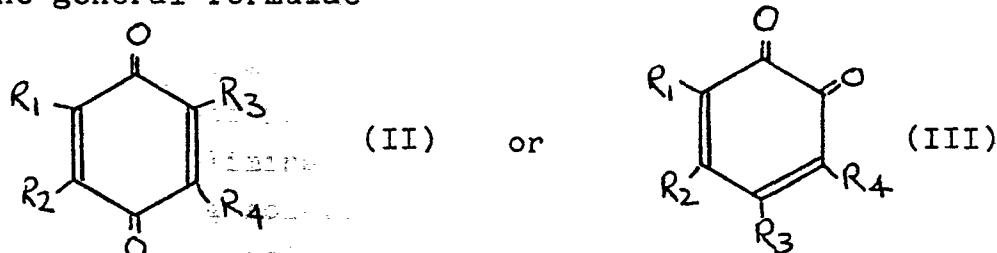
Sets of DI cans were sprayed with cleaning solutions 15s, 16s and 17s, one set per test, at solution temperatures of 124°F (&51°C) for the times indicated; and the results obtained are summarized in Table XI as follows :

TABLE XI

<u>Cleaning Solution</u>	<u>Treatment Time</u>	<u>Observed Result</u>
15s	1 minute	No de-tinning; bright, rust-free surface; water-break-free cans
16s	1 minute	No de-tinning; bright, rust-free surface; water-break-free cans
17s	1 minute	Spotty Whitening; some de-tinning
15s	30 minutes	No de-tinning; bright, rust-free surface; water-break-free cans
16s	30 minutes	No de-tinning; bright, rust-free surface; water-break-free cans
17s	30 minutes	Badly mottled dark surface; severe de-tinning

CLAIMS

1. An aqueous alkaline cleaning solution for removing lubricants or other soiling contaminants from a tin surface without visibly etching it, said solution having a pH in the range of from about 11 to about 13 and containing effective amounts of an alkaline component and of an inhibitor, characterized in that the inhibitor is or includes one or more substituted or unsubstituted quinones and/or substituted or unsubstituted polyhydroxybenzenes.
2. A cleaning solution as claimed in claim 1, characterized in that the inhibitor is or includes a substituted quinone and/or a substituted polyhydroxybenzene wherein the substituent(s), besides the hydroxy substituent on the benzene ring, include a halo, alkyl, alkoxy, carboxyl, nitro and/or cyano substituent.
3. A cleaning solution as claimed in claim 1 or claim 2, characterized in that the inhibitor is or includes a substituted or unsubstituted quinone conforming to one of the general formulae



in which R_3 and R_4 , which may be the same or different, each represents a hydrogen atom or a hydroxy, halo, alkoxy, alkyl, carboxyl, nitro or cyano group; and either R_1 and R_2 which may be the same or different each represents at atom or group as defined for R_3 and

R_4 or together R_1 and R_2 constitute an alkyldienyl group which in turn, together with the quinone ring to which they are attached, forms a naphthaquinone.

4. A cleaning solution as claimed in claim 3, characterized in that the inhibitor is or includes 1,4-benzoquinone and/or 1,2-benzoquinone and/or α -naphthaquinone and/or β -naphthaquinone.

5. A cleaning solution as claimed in claim 1 or claim 2, characterized in that the inhibitor is or includes one of the following substituted or unsubstituted polyhydroxybenzenes, namely catechol (ortho-dihydroxy benzene) and/or resorcinol (meta-dihydroxy benzene) and/or hydroquinone (1,4-dihydrobenzoquinone or para-dihydroxy benzene) and/or hydroxy-hydroquinone (1,2,4-trihydroxybenzene) and/or 1,3,5-trihydroxy-benzene and/or gallic acid (3,4,5-trihydroxy benzoic acid) and/or 1,2,4,5-tetrahydroxy-benzene.

6. A cleaning solution as claimed in any of the preceding claims, characterized in that the inhibitor is present in a concentration in the range of from about 0.02 g/l to about 0.06 g/l.

7. A cleaning solution as claimed in any of the preceding claims, characterized in that it also includes a polyelectrolyte in a concentration effective substantially to prevent precipitation of calcium and/or magnesium ions causing water-hardness.

8. A cleaning solution as claimed in claim 7, characterized in that the polyelectrolyte is present in a concentration of at least about 0.1 g/l.

9. A cleaning solution as claimed in any of the preceding claims, characterized in that the alkaline

component therein consists of one or a mixture of more than one alkali metal hydroxides and/or alkali metal carbonates and/or alkali metal silicates and/or ammonium hydroxide and/or ammonium carbonate.

10. A process for removing lubricants or other soiling contaminants from a tin surface without visibly etching it, in which the surface is brought into contact for a sufficient time at the chosen temperature with an aqueous alkaline cleaning solution, as claimed in any of the preceding claims, characterized in that the temperature employed is in the range of from about 100° to about 130°F (approx. 38°C to 54°C).

11. A process as claimed in claim 10, characterized in that it includes the preliminary step of making-up the aqueous alkaline cleaning solution by dissolving from about 3 g/l to about 7 g/l of a solid cleaning composition in water, at least 15% by weight of the composition being formed by the alkaline component and at least about 0.1% by weight of the composition being formed by the inhibitor, said composition also optionally including a polyelectrolyte in a proportion effective substantially to prevent precipitation of calcium and magnesium ions in hard water.

12. A process as claimed in claim 10, characterized in that it includes the preliminary step of making-up the aqueous alkaline cleaning solution by dissolving from about 0.5% to about 2% by volume of an aqueous concentrate in water, said concentrate containing up to 770 g/l of the alkaline component and at least about 2 g/l of the inhibitor, as well as optionally a polyelectrolyte in a proportion effective substantially

to prevent precipitation of calcium and magnesium ions in hard water.

13. A solid cleaning composition, for use in the process of claim 11, characterized in that it comprises at least 15% by weight of an alkaline component and at least about 0.1% by weight of an inhibitor which is one or more substituted or unsubstituted quinones and/or substituted or unsubstituted polyhydroxybenzenes, as well as optionally an effective amount of a polyelectrolyte.

14. An aqueous concentrate, for use in the process of claim 12, characterized in that it comprises up to 770 g/l of an alkaline component and at least about 2 g/l of an inhibitor which is one or more substituted or unsubstituted quinones and/or substituted or unsubstituted polyhydroxybenzenes, as well as optionally an effective amount of a polyelectrolyte.



DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
D, X A	CH - A - 252 362 (CIBA AKTIENGESELLSCHAFT) + Page 1, lines 20-37; claims + --	1, 2, 5	C 23 G 1/20 C 23 G 1/18
	US - A - 2 710 843 (L.F. STEBLEON) + Claims + --	1	
	US - A - 4 094 701 (FEKETE) + Claims + --	1, 2, 5	
	O-A. NEUMÜLLER "Römpps Chemie-Lexikon" 7 th edition, 1977 FRANCKH'SCHE VERLAGSHANDLUNG, Stuttgart page 3462 -----		TECHNICAL FIELDS SEARCHED (Int. Cl.) C 23 G
			CATEGORY OF CITED DOCUMENTS X: particularly relevant A: technological background O: non-written disclosure P: intermediate document T: theory or principle underlying the invention E: conflicting application D: document cited in the application L: citation for other reasons &: member of the same patent family, corresponding document
X	The present search report has been drawn up for all claims		
Place of search	Date of completion of the search	Examiner	
VIENNA	19-08-1981	SIAMA	