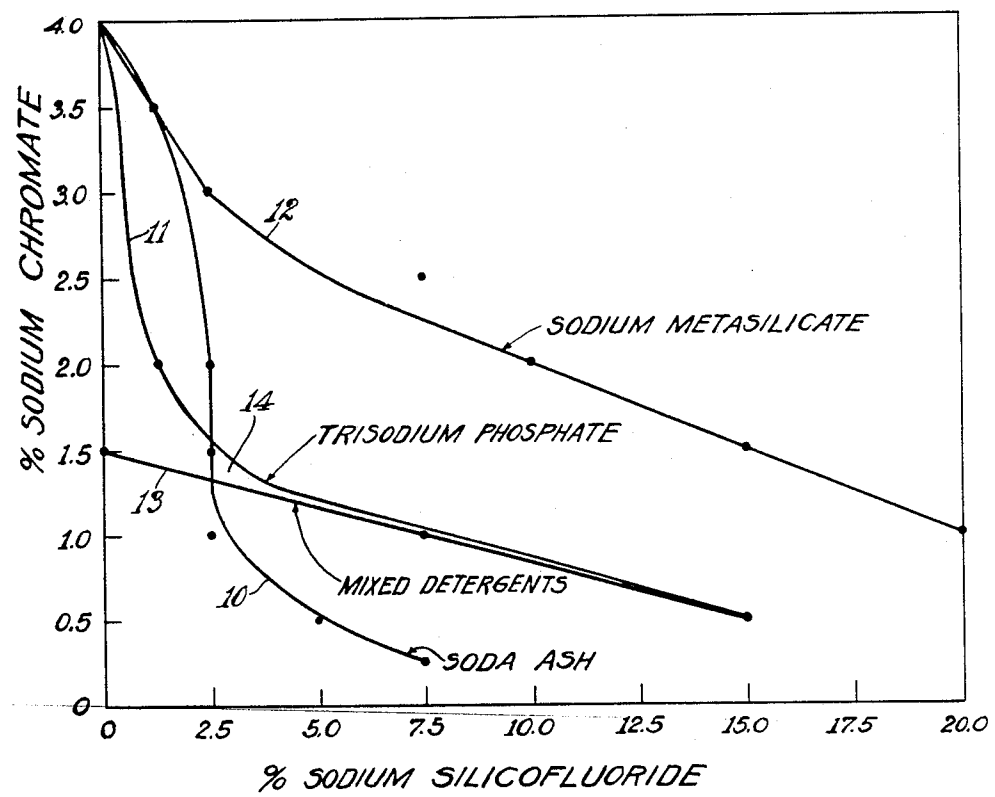


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DETERGENT COMPOSITION
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Fig.1



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DETERGENT COMPOSITION

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The present invention relates to cleaning tin surfaces, particularly on food containers, such as milk cans, pie tins, bread tins, cake tins, meat-loaf tins, and the like. These so-called "tins" are commonly sheet iron articles with a tin coat, which when new is shiny and uniformly mirror-like in appearance.

In commercial cleaning of such articles an alkali detergent solution is used. It has long been known that such solutions corrode the tin and produce "spangling," the latter being a crystal growth which destroys the mirror-like surface. The spangled surface resembles the frosty-like appearance of new galvanized iron articles. The appearance of spangling is an indication that the tin surface is on the way to destruction. Heretofore, many addition agents have been successfully used to inhibit the corrosion and spangling. Among these, one of the most successful is an alkali metal chromate, usually sodium or potassium chromate, or dichromate in the dry composition before solution in water. These are commonly provided as solid or dry compositions which are sold to be added in specified quantity to water, for a commercial cleaning bath, which is commonly heated to 80° C. to boiling temperatures. Dichromate in the composition, in an alkaline solution becomes chromate. Chromates and dichromates are comprehended within the broader term "a chromate."

The primary disadvantage of chromates is an injurious action on the hands, which generally come in contact with the bath in a large number of establishments where such compositions are used. The amount required for inhibiting effect makes the composition an objectionable one. The dry compositions commercially have about 5% of sodium chromate, in spite of the fact that the Kochs Patent No. 1,962,821 sets forth compositions from 1% to 8% where an alkali metal silicate is also present as a part of the alkali detergent.

The present invention aims to reduce the chromate content to 3% and preferably to below 1%, by the addition of another agent which is effective to cause the lower chromate content to exhibit an inhibiting action at least equivalent to and better than that of the prior art commercial chromate-inhibited detergents.

In particular, it is an object of the invention to use alkali-metal silicofluoride as the said added agent to render a composition with small quantities of chromate at least equivalent in inhibiting effect to compositions with larger quantities of chromate.

In experiments to develop alkaline cleaning baths for tin, it was discovered that sodium or potassium silicofluoride in the composition, undergoes a change in alkali solution, which change is beneficial to the action of cleaning compositions. It is known for example, that sodium silicofluoride in alkali solution decomposes into sodium fluoride and a form of silica, as a colloidal suspended silica compound. In experimenting with various successful compositions in which sodium silicofluoride is an ingredient, modifications have been made, limited to the sodium silicofluoride in order to determine why the sodium silicofluoride functions. Omitting it renders the compositions ineffective. Adding an equivalent amount of sodium fluoride renders the composition ineffective, showing that the effect is not attributed to the sodium fluoride formed with the alkali detergent. Also, adding an equivalent of freshly precipitated silica (adding first acid and then ammonia to a sodium metasilicate) is not the equivalent of using the sodium silicofluoride. The same is true with respect to silica gel and silicic acid. When the equivalent amounts of sodium fluoride and freshly precipitated silica were used, the effect was not the same as with sodium silicofluoride.

Then tests were made to determine whether the sodium silicofluoride lowered the buffer index of the composition, by adding hydrochloric acid equivalent to the sodium silicofluoride. This did not explain the action. Finally, the effect could be obtained in only two ways: (1) by having sodium silicofluoride present in the dry composition, and (2) by adding sodium silicofluoride to a bath containing the other ingredients. It therefore appears that silicofluoride must form one or more kinds or forms of reaction products which are effective only in the solution where formed. This is confirmed by the fact that the cleaning bath must be used with or after agitation to make certain that any solid or settled ingredients in the bath dissolve in whole or in part at an equilibrium condition for the temperature of the bath.

In chromate-inhibited detergents containing the products from sodium silicofluoride, a much lower amount of chromate may be used. A composition containing 5% chromate without the sodium silicofluoride can be altered to have but 0.5% chromate without loss of inhibited effect, when 5% to 15% of sodium silicofluoride is also used, depending upon the character of the alkali. Thus, the bath may be made far less injurious to the hands, and may be compounded at less cost.

The use of alkali metal silicates is not the equivalent of the sodium silicofluoride to reduce the chromate requirements, as will be shown by the following explanation.

Commercial practice in the use of alkaline detergents is more or less standardized at specifying up to and not over 8 ounces of the solid chemical composition per gallon of water, and use at 80° C. to boiling. These requirements have been observed for test purposes, using, however, boiling solutions to standardize on temperature and to maintain agitation. Loss of water in the tests was avoided by use of reflux apparatus. A very severe test has been imposed to define successful and unsuccessful solutions.

Baking tins present a more severe requirement than milk cans, for example. Milk cans present a polished metallic tin surface. Baking tins when new, have such a surface which is not desired by bakers. It acts as a reflective insulation retarding baking. It is customary for bakers to heat-treat new tin-ware to produce an amber-colored bronze-like, so-called "burned-on" coat, which is believed to be an oxide film. This may be produced by heating the new tins in an oven at 375°-400° F. for one-half hour to one hour. Bakers not only desire to prevent spangling of the tin, but also to retain this coat in using alkaline cleaning baths.

Another feature of a successful composition is the ability to use the bath more than once. In other words, its inhibiting qualities must not vanish early. Freshly made compositions which are successful to clean and preserve the burned-on coat of a first insert, and which then remove the coat from a following insert, are considered to be unsuccessful compositions.

In determining the line between successful compositions and unsuccessful compositions, as defined for the present invention, the following test has been employed.

A bath is prepared in the proportion of 8 ounces of the composition to be tested to 1 gallon of water. A 100 cc. volume of the solution is heated to boiling under reflux conditions in a glass flask. Test strips are fresh tinned sheet iron $\frac{3}{4} \times 3$ inches with and without burned-on coating on both sides. These present galvanic couples as well as full-tinned areas, and the couples introduce electrical forces which the cleaning bath must make non-corrosive in actual effect. One strip is immersed for 1 hour. If it is injured the composition is deemed not satisfactory. If it is not injured, another strip is inserted for 5 hours. If it is injured, the composition is deemed not satisfactory. If it is not injured, another strip is inserted for 15 hours. If it is injured, the composition is deemed not satisfactory. If it is not injured the composition is deemed successful and satisfactory.

Upon this basis many compositions have been tested using as the principal alkaline agent (1) anhydrous soda ash, (2) crystalline trisodium phosphate with 12 molecules of water, (3) sodium metasilicate, and (4) a mixture of equal parts of the first three. These are the common non-caustic alkaline detergents, although the art is not limited to them. Various percentages of sodium chromate, and various percentages of sodium silicofluoride were present. Since sodium silicofluoride consumes alkali in the decomposition occurring in tests, change of alkalinity or alkaline base was avoided by adding also just enough caustic soda to supply the alkali consumed.

Fig. 1 represents the limiting lower percentages of sodium chromate and of sodium silicofluoride in the compositions indicated.

At 4% of sodium chromate and with no sodium silicofluoride, where the detergent is soda ash, or is trisodium phosphate, or is sodium metasilicate, it is shown that the compositions are satisfactory. Where the detergent is the mixture of these three, 1.5% of sodium chromate with no sodium silicofluoride, makes a satisfactory composition. It is also shown that as sodium silicofluoride is added, the amount of chromate may be reduced. In the case of soda ash, illustrated by line 10, 1.5% of sodium silicofluoride displaces about 0.5% of the composition as sodium chromate, and 2.5% of sodium silicofluoride displaces about 3% of the composition as sodium chromate, and beyond this point, the additional silicofluoride is less effective. However, 5% of sodium silicofluoride displaces $3\frac{1}{2}$ % of the composition as sodium chromate, and 7.5% of sodium silicofluoride displaces 3.7% of the composition as sodium chromate.

In the case of trisodium phosphate, the effect of small amounts of sodium silicofluoride is shown by line 11 to be still more effective in displacing sodium chromate than in the case of soda ash of line 10, but the effect falls off earlier, and at about 2.5% sodium silicofluoride, about 2.5% of the composition as sodium chromate is displaced. To reduce the chromate respectively to 1% and 0.5%, the sodium silicofluoride is 7.5% and 15%.

In the case of sodium metasilicate as shown by line 12, the effectiveness of the sodium silicofluoride is still less, and 2.5% of it displaces about 1% of the composition as sodium chromate, and 15% of it displaces about 2.5% of the composition as sodium chromate.

In the case of the mixed detergents as represented by line 13, the effect is much less. However, since this mixture permits of less chromate when no silicofluoride is present, it may be said more favorably that this necessary chromate may be cut in half by about 11% of sodium silicofluoride.

EXAMPLES

The curves 10 to 13 show many compositions within the invention. However, the invention is not limited to the alkaline detergent bases disclosed, and it is to be understood that other mixtures may be used, such as

Example 1

	Per cent
Soda ash	19.5
Trisodium phosphate, monohydrate	45
Sodium metasilicate	25
Sodium silicofluoride	10
Sodium bichromate	0.5

Example 2

	Per cent
Soda ash	44.5
Sodium metasilicate	50
Sodium silicofluoride	5
Sodium bichromate	0.5

It will be noted that the region where lines 10, 11, and 13 lie close together is designated 14, and it corresponds substantially to about 1.5% chromate and about 2.5% silicofluoride. For the detergent bases of these lines 10, 11 and 13, compositions having at least about 1.5% and less than 4% chromate, and at least 2.5% silicofluoride are

satisfactory, and in them, if the silicofluoride is increased the chromate may be reduced.

It is also observed that in the series of curves, after any knee thereof is passed with increasing amounts of the silicofluoride, the lines are generally parallel, with the slope of lines 11 and 13 being the approximate slope. According to this indication, every increase of 1% in the silicofluoride corresponds to about .075% permissible decrease in chromate from a critical lower limit according to the test used. This applies generally after the silicofluoride content reaches 2.5%, showing that this is a critical lower limit for the silicofluoride above which its function is fairly constant. At this critical limit, the chromate must be about 1.5% for all the detergents shown, except that it must be about 3% for sodium metasilicate on curve 12.

It is not necessary to provide the chemicals as a mixture. It is permitted also to add the silicofluoride as a separate ingredient to a bath containing the chromate and alkali, or to contain one or both of them. For example, a bath or composition of alkali and chromate insufficient to inhibit injury, and in excess of 0.3 to 0.5% of the chemicals of the bath, may be made inhibitory by adding sufficient alkali metal silicofluoride as herein disclosed.

Numerous variations of the invention will occur to those skilled in the art from the description and from the illustration, and such are contemplated as falling within the scope of the appended claims.

We claim:

1. An alkaline composition for forming cleaning baths for metal-ware with tin surfaces comprising as the essential cleaning constituent a non-caustic alkaline detergent, less than 4% of a chromate salt of alkali metal, and an alkali metal silicofluoride up to about 15%.

2. An alkaline composition for forming cleaning baths for metal-ware with tin surfaces comprising as the essential cleaning constituent a non-caustic alkaline detergent, from 4% to 1.5% of an alkali metal chromate, and up to 15% of alkali metal silicofluoride, the quantity of chromate being greater when the quantity of the silicofluoride is lesser.

3. An alkaline composition for forming cleaning baths for metal-ware with tin surfaces comprising as the essential cleaning constituent a non-caustic alkaline detergent, at least 1.5% and not more than 4% of alkali metal chromate, and at least 15% of alkali metal silicofluoride.

4. An alkaline composition for forming cleaning baths for metal-ware with tin surfaces comprising as the essential cleaning constituent trisodium phosphate, less than 4% and at least 0.5% to 1.5% of alkali metal chromate, and from 15% to about 2.5% of alkali metal silicofluoride, the higher quantity of the silicofluoride being used for the lowest quantity of the chromate and the lower quantity of the silicofluoride being used when there is at least about 1.5% of chromate.

5. An alkaline composition for forming clean-

ing baths for metal-ware with tin surfaces comprising as the essential cleaning constituent substantially equal parts of soda ash, trisodium phosphate and sodium metasilicate, less than 4% and at least 0.5% to 1.5% of alkali metal chromate, and from 15% to about 2.5% of alkali metal silicofluoride, the higher quantity of the silicofluoride being used for the lowest quantity of the chromate and the lower quantity of the silicofluoride being used when there is at least about 1.5% of chromate.

6. An alkaline composition for forming cleaning baths for metal-ware with tin surfaces comprising as the essential cleaning constituent soda ash, less than 4% and at least from about 0.3% to about 1% of alkali metal chromate, and from about 7.5% to about 2.5% of alkali metal silicofluoride, the higher quantity of the silicofluoride being used for the lowest quantity of the chromate and the lower quantity of the silicofluoride being used when there is at least about 1% of chromate.

7. An alkaline composition for forming cleaning baths for metal-ware with tin surfaces comprising as the essential cleaning constituent soda ash, less than 4% and at least about 0.3% of alkali metal chromate, and alkali metal silicofluoride up to at least 7.5%, chromate in the range of 3.5% to about 1% corresponding to silicofluoride at least in an amount in the range from 1.5% to 2.5%, and chromate in the range from 1% to 0.3% corresponding to silicofluoride at least in the range from 2.5% to 7.5%.

8. An alkaline composition for forming cleaning baths for metal-ware with tin surfaces comprising as the essential cleaning constituent a non-caustic alkaline detergent, at least 2.5% of alkali metal silicofluoride, and less than 4% and at least from 1.5% to 3% of alkali metal chromate, the quantity within the said range of 1.5% to 3% being dependent upon the alkali detergent such that when it is sodium metasilicate the chromate is at least 3%.

9. An alkaline composition for forming cleaning baths for metal-ware with tin surfaces comprising as the essential cleaning constituent a non-caustic alkaline detergent, at least 2.5% of alkali metal silicofluoride and at least a critical inhibiting amount of alkali metal chromate and less than 4%, the highest critical amount corresponding to 2.5% of the silicofluoride, and the said highest critical amount being reduced by about .075% in the composition for each increment of 1% in the content of the silicofluoride.

10. An alkaline composition for forming cleaning baths for metal-ware with tin surfaces comprising as the essential cleaning constituent a mixture of substantially equal parts of soda ash, trisodium phosphate, and sodium metasilicate; and less than 4% of alkali metal chromate, and up to 15% alkali metal silicofluoride, the lower limit of chromate being from 1.5% to 0.5% accordingly as the silicofluoride varies from 15%.

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