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INHIBITED DETERGENT COMPOSITION

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The present invention relates to alkaline detergent baths and compositions to produce the same, useful particularly for cleaning metal surfaces of tin, zinc, iron or aluminum, without deleterious action such as corrosion, dissolution, "spangling", or checking.

In our prior application Serial No. 66,436, filed February 29, 1936, we have described and claimed compositions of matter involving water-soluble ingredients which may be taken up in water to produce the desired cleaning bath. The present application is generic to said prior application, and is a continuation in part thereof. It aims to disclose mixtures in which the ingredients are not all of the water-soluble type, which may be acted upon by water to produce a solution of the same general nature for use as the cleaning bath. Fundamentally, the utility of the invention is in the bath, wherein water predominates. Commercially, however, the bath is not a satisfactory article of commerce, so the ingredients minus the water are compounded for sale. The most practical composition involves water-soluble constituents as taught in said prior application. The present application shows that the ultimate result may be accomplished by use of different compositions.

The use of alkaline agents is well known for cleaning metal ware of zinc, aluminum or tin plate, such as milk cans, baking pans, etc., which have oil, grease or fat, burned-on flour, milk curds, etc. It is realized that baths of these agents are usually injurious to the metal in the concentrations and at the elevated temperatures and the time of action ordinarily employed. It is also known that inhibiting agents are added to minimize or prevent such deleterious action. Some of these inhibited detergent compounds are effective when the metal pieces are washed in wooden, glass or enamel tanks or under other conditions which do not produce additional deleterious influences. For example, there may be found baths which are effective in a glass tank, but which are not effective in a galvanized iron tank, or in an iron tank, when the metal being cleaned is in contact with the metal of the tank. The tank metal and the metal piece to be cleaned establish electrical contact and are in a common bath, thus establishing galvanic action. By this condition different electrical potentials between the two metals and the solution cause a galvanic flow of electricity, or alteration of the single potential which exists between each metal alone and the cleaning bath. The same conditions may occur in a non-conductive tank where

different kinds of metal pieces are being cleaned in contact with each other. The alteration of conditions as a result of these galvanic couples can be sufficient to produce corrosion or injury with cleaning baths which are otherwise satisfactory.

The present invention aims to produce a detergent compound which is more universally effective for various metals to be cleaned, and for use in glass, zinc, galvanized iron, or iron tanks, and for use simultaneously with different metals to be cleaned. It is an object to provide a compound in solid form to be added to water to form a bath, or else to provide the bath itself. Although the invention provides a bath which is effective where galvanic force exists, it should be understood that the conditions which are encountered in the galvanic action are the result of forces which exist in the absence of a galvanic couple, namely the electrical potential existing between the bath and the metal to be cleaned. This potential is involved in the deleterious action to be avoided. The bath, therefore, as a whole, creates a favorable single potential between the bath and the metal, which potential is such that it remains favorable when galvanic conditions are also encountered.

The detergent compounds in this art are generally used in concentrations varying from $\frac{1}{2}$ to 8 ounces per gallon, and in the work leading to this invention this range of concentration has been more particularly studied. The general statements herein made are with reference to such a range of concentration, but it is not to be assumed that the general statements are not applicable above and below this range. The temperature and time of exposure to the cleaning agent also have a bearing on the action, and unless otherwise specified general statements are to be considered with reference to conditions commonly encountered in commercial practice.

Common alkaline reacting detergents are soda ash, water soluble inorganic alkaline detergents, caustic soda, tri-sodium phosphate, sodium silicate, borax, etc. Several of these may be used in weak solutions, such as 0.15% to .3% concentration when cold without giving corrosion, or other deleterious action, but the cleaning action is not effective. When heated to secure effective cleaning, there is also corrosion or other adverse action. Addition agents for inhibiting corrosion are recognized but they have limited or specific action depending upon concentration and kind of alkali, concentration of inhibiting agent, temperature, and time. Sodium hypochlorite is one

such agent. Chromates are recognized inhibitors for mild alkaline detergents. Perborates have been used. Hypochlorites are also known. By some it is considered that the function of such inhibitors is the same because these are oxidizing agents. However, we have established that this is not true.

Calcium hypochlorite is not a successful inhibitor for use with the general run of alkaline detergents when used for tin or aluminum surfaces, and for use in glass, iron, zinc or galvanized tanks. Neither are zinc salts, such as zinc sulphate, suitable inhibitors under these conditions. The present invention is based upon the discovery that calcium hypochlorite and zinc salt such as zinc sulphate, may be used in combination as a corrosion inhibiting mixture for alkaline detergents under the described conditions.

The invention appears to involve the essential combination of hypochlorite ions and zinc ions in the solution, where detergent alkali is present. We have found that perborate is not an equivalent of hypochlorite in the invention. For example to a composition:

	Parts by weight
Trisodium phosphate monohydrate.....	42.5
Soda ash.....	42.5
Anhydrous zinc sulphate.....	10
we have added:	
Case A—sodium perborate.....	5
and	
Case B—high test calcium hypochlorite....	5

Case A.—The composition at a concentration of 2 ounces per gallon shows no corrosion on tin and aluminum in 48 hours at 70°-75° F., but at the boiling temperature it shows heavy corrosion on tin in 1 hour and 10 minutes, and on aluminum in 15 minutes.

Case B.—At the same concentration as Case A, the bath at 70°-75° F. shows no corrosion on tin and aluminum in 48 hours, while at boiling temperatures no corrosion of tin occurs, yet there is corrosion of aluminum. However, the protection of aluminum depends upon the use of another ingredient, namely, sodium silicate, yet in this instance, the perborate is not an equivalent of hypochlorite as shown by the following:

	Parts by weight
Trisodium phosphate monohydrate.....	25
Soda ash.....	39.75
Sodium metasilicate (Metso).....	20
Anhydrous zinc sulphate.....	10
we have added:	
Case C—sodium perborate.....	5
and	
Case D—high test calcium hypochlorite....	5

At concentrations of 2 ounces per gallon, Case C shows no corrosion on tin and aluminum at 70°-75° F. in 48 hours, while a boiling solution shows heavy corrosion of tin in 10 minutes, and on aluminum in 1 hour; and Case D shows no corrosion on tin or aluminum in cold or boiling solution in 48 hours.

We believe that these oxidizing agents differ because perborate on heating loses oxygen which readily escapes, while hypochlorites on heating lose chlorine, which is highly soluble. The hypochlorites provide complex oxygen-chlorine radicals which are somewhat unstable in solutions limited to alkali metal and alkali earth cations, but which seem to be far more stable when zinc ions are present. Zinc has the faculty of forming

stable compounds with both oxygen and chlorine. Therefore, we believe that the presence in the bath of zinc cations and of hypochlorite ions results in a combination making the bath a successful corrosion inhibiting alkaline bath.

In addition to the examples Case B and Case D of the invention wherein water-soluble constituents are used (our prior application), the following examples are given to show the use of water-insoluble zinc compounds which become soluble in a bath in the presence of the companion ingredients of the examples, sufficiently to provide the desired inhibiting action.

EXAMPLE E

	Parts by weight
Trisodium phosphate monohydrate.....	32.50
Soda ash.....	32.25
Sodium metasilicate.....	20
High test calcium hypochlorite.....	5
Zinc hydroxide.....	10
Wool orange 2-G.....	.25

EXAMPLE F

In Example E the same weight of zinc carbonate is used in place of zinc hydroxide.

EXAMPLE G

(Example 2 of the prior application)

	Parts by weight
Trisodium phosphate monohydrate.....	30
Anhydrous sodium carbonate.....	39.75
High test calcium hypochlorite.....	6
Anhydrous zinc sulphate.....	9
Sodium metasilicate.....	15
Wool orange 2-G.....	.25

EXAMPLE H

Zinc hydroxide is substituted for zinc sulphate in Example G.

EXAMPLE I

Zinc carbonate is substituted for zinc sulphate in Example G.

EXAMPLE J

(Example 4 of prior application)

	Parts by weight
Borax.....	24.75
Sodium metasilicate.....	15
Anhydrous sodium carbonate.....	45
High test calcium hypochlorite.....	5
Anhydrous zinc sulphate.....	10
Wool orange 2-G.....	.25

EXAMPLE K

Zinc oxide replaces zinc sulphate in Example J.

EXAMPLE L

Zinc hydroxide replaces zinc sulphate in Example J.

EXAMPLE M

Zinc carbonate replaces zinc sulphate in Example J.

EXAMPLE N

(Example 5 of prior application)

	Parts by weight
Trisodium phosphate monohydrate.....	25
Anhydrous sodium carbonate.....	39.75
Sodium metasilicate.....	20
High test calcium hypochlorite.....	5
Anhydrous zinc sulphate.....	10
Wool orange 2-G.....	.25

EXAMPLE O

Zinc hydroxide replaces zinc sulphate in Example N.

EXAMPLE P

Zinc carbonate replaces zinc sulphate in Example N.

EXAMPLE Q

(Example 1 of prior application)

	Parts by weight
Trisodium phosphate monohydrate	32.50
Anhydrous sodium carbonate	32.25
Sodium metasilicate	20
Calcium hypochlorite (70-72% available chlorine)	5
Anhydrous zinc sulphate	10
Wool orange 2-G	25

EXAMPLE R

Zinc oxide replaces the zinc sulphate of Example Q.

EXAMPLE S

Zinc hydroxide replaces the zinc sulphate of Example Q. This composition is like Example E.

EXAMPLE T

Zinc carbonate replaces the zinc sulphate of Example Q. This composition is like Example F.

EXAMPLE U

Zinc hydroxide replaces the zinc sulphate of Case B above.

EXAMPLE V

Zinc carbonate replaces the zinc sulphate of Case B above.

EXAMPLE W

In any of the foregoing 5 parts of calcium hypochlorite (70-72% available chlorine) is replaced by 6 parts of sodium hypochlorite $\text{NaClO} \cdot 2\frac{1}{2}\text{H}_2\text{O}$. Thus in Example G, 7.2 parts of the sodium hypochlorite is used.

It will be observed from the above formulas that the composition is solid, being a mixture of the separate ingredients named. These are to be used in concentrations of $\frac{1}{2}$ to 8 ounces per gallon of water. The resulting bath is not necessarily a solution of these ingredients unchanged. It must be recognized that there may be reactions between ingredients when water is present, that new compounds are formed; that even precipitates may be formed; that the solution arrives at some equilibrium composition at definite conditions and is variable with change of conditions; and that in use this bath may change considerably in its composition. Precipitates may not form in making a solution, but may tend to form, and they may form in use of the bath for cleaning.

The inhibiting action may be due to formation of an inhibiting film on the metal, or to the tendency to form an inhibiting film. Frequently in chemical action there is a force tending to produce a certain result. The action does not occur until a certain "threshold" value of the force is attained, yet the mere existence of the force without a visible result therefrom, is a vital factor in a process.

Such a condition has been observed in studying the present invention, but there is reason to believe that it is not the only instance of such conditions. This observation relates to the presence of zinc in the bath.

There have been observed certain conditions under which zinc from the solution plates out, electrochemically or galvanically, onto the metal being cleaned. This indicates that a certain "threshold" value for a zinc-depositing force has been exceeded, resulting in the zinc deposition. On the low side of this limiting value for the force, the tendency for zinc to plate out must exist, yet the zinc does not deposit visibly. It may be depositing invisibly at a rate equal to or less than a rate at which it is dissolved, so that the net result is no deposition.

It is well recognized that where there is a tendency to plate onto a metal, there is little or no tendency for the metal to be dissolved by the plating solution. From these facts and observations it is believed that the presence of zinc in the solution is an important factor contributing to the inhibiting action of the composition. It is quite likely that the zinc in solution acts to alter the potential difference between the bath and the metal to be cleaned, from what the potential would be if the zinc were absent. However, the action of the soluble zinc appears to be joint with other ingredients.

Alkaline detergent part

The invention may be practiced with the common alkaline detergents, but it is preferred that the less caustic ones be used, in order to protect workers from caustic burns. Mixed alkaline detergents are preferred, and a fine mild combination consists of trisodium phosphate monohydrate, anhydrous sodium carbonate (soda ash) and sodium metasilicate ($\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$). This mixture in the present invention has the advantage of protecting iron, zinc, tin and aluminum surfaces. Borax may be substituted for the trisodium phosphate monohydrate for the protection of these metals. Where sodium metasilicate is omitted from the mixture of alkalis, the composition does not protect aluminum, but it does protect the zinc, iron and tin surfaces. Those compositions not having the silicate are not effective on aluminum under the regular condition of commercial usage. The alkaline detergent part of the whole composition may vary in a wide manner. In the final composition the alkaline detergent part is preferably 85% where the inhibiting part is about 15%. The exact ratio is not critical and the variations may be readily determined by simple experimentation. Sodium silicate is primarily of the alkaline detergent part, but as to aluminum it also falls in the inhibiting part. There are several forms of sodium silicate, and their specific effects may vary the efficiency or limiting proportions for a given set of conditions. The sodium metasilicate is preferred to others, such as sodium orthosilicate because in the dry solid composition it creates better stability.

Inhibiting part

The inhibiting portion of the mixture consists of the water soluble hypochlorite salt and the zinc compound. The latter may be water soluble, such as zinc sulphate or zinc acetate, or water-insoluble, such as zinc oxide, zinc hydroxide or zinc carbonate. All these zinc compounds readily dissolve in the resulting bath to a sufficient extent to provide zinc in solution. Because metallic zinc can be deposited, we believe it must be present as a cation.

In the bath, the essential inhibitors are the zinc in solution and in equilibrium with any zinc in suspension, and the hypochlorite salt. In

making the bath directly, various compounds may be used. The two inhibiting ingredients may vary in their ratio to each other, and there will of course be one ratio which is more effective for a certain alkaline agent or combination of them. This efficient ratio may also vary for the conditions of use, and with variations in the ratio between the alkaline part and the inhibiting part. It is therefore not possible to set forth explicitly a definite efficient ratio.

The commercially preferred ratio and form is 1 part of calcium hypochlorite (high test commercially defined as having 70 to 72% available chlorine and containing about 3% of calcium chloride and 23% sodium chloride) and 2 parts of anhydrous zinc sulphate (about 36% zinc content) or its equivalent. For 85% content of the preferred alkaline mixture above described, and 15% content of inhibiting part, the latter has the preferred ratio of 1 part of commercial "high test" calcium hypochlorite and 2 parts of anhydrous zinc sulphate. If this last ratio is reversed the desired effect is not obtained. The critical limit is not subject to determination unless exact specifications for use are given, and then there must be considered the extent to which the bath is allowed to deteriorate in use, before it is considered non-effective.

The important ingredient in the commercial high test calcium hypochlorite is the combination or compound of calcium, oxygen and chlorine. The sodium chloride present in the form described is not any essential part of the invention, but its presence obviously plays a part in determining critical proportions of the essential ingredients for any set of conditions. There are on the market various forms of "high test calcium hypochlorite", and in addition to the form having sodium chloride, there is a form having calcium chloride instead of sodium chloride. This may be used in the composition with appropriate adjustments, but it is not preferred where a solid powder is marketed on account of the hygroscopic nature of calcium chloride. There are also available solid sodium hypochlorites which may be used, as well as sodium hypochlorite solutions that may be employed.

The examples

The examples show wool orange 2-G, but this is merely an example of a dyestuff optionally added to give character or distinction to the composition and to the bath.

All the examples give adequate protection to iron, zinc, and tinned ware. Formulas having sodium silicate are adequate for iron, zinc, aluminum and tinned ware. These formulas give such protection when the temperature is maintained above 80° C. or higher and at the boiling point for extensive periods of time longer than commercially used to effect cleaning, such as 8 hours and even to 48 hours. The effectiveness of the inhibitor may be appreciated by the fact that any of the alkaline agents alone in the same concentration (such as 85% of the 1/2 to 8 ounces per gallon) at 70° C., give corrosive action on both aluminum and tinned ware in a few minutes, and immediately at 100° C. If hypochlorite is left out, all will corrode the metals.

The formula of Case B is exceptional in that it will deposit zinc upon tinned ware when the concentration is too high, for example over about 5 ounces per gallon. This is striking evidence of a function for zinc in the bath, at lower concentrations where it is not deposited. The tendency

to deposit is no doubt an important part of the inhibiting forces.

Examples Q to T are given to represent a special condition of use wherein the resulting bath has been used at temperatures above 80° C. but without boiling. There is initially, or is developed in use, a suspended precipitate which in boiling is agitated to come into contact with metal being cleaned. Where no boiling takes place this settles, and to avoid contact with the metal the parts being cleaned were suspended above the settled precipitate. In three hours heating there is no corrosion but a slight white precipitate forms on the metal which is easily removed. These and the other examples give no corrosion under boiling conditions.

The composition is preferred in a form which may be economically marketed. Hence ingredients are chosen which may be mixed to remain stable and non-reactive. The available chlorine from the hypochlorite may be fugitive and its retention is important. Absence of water is desirable to keep the mass stable. Steel drums are suitable containers for inducing stability in the compositions given. Although there may be water of crystallization in some of the components (particularly the borax, and the trisodium phosphate monohydrate) it is so closely bound that it is not detrimental to stability.

When the composition is dissolved reactions occur which vary with the composition and conditions. The bath may even become milky with some precipitate or insoluble suspension. Transient films may be formed on the metal to be cleaned, yet the cleaning action without deleterious action on the metal is effected. The baths may be boiled, for example for 8 hours, with little loss of available chlorine. The bath itself is stable at the commercially useful dilution.

It is to be understood that the bath itself is the functioning composition of the invention, and that it may be described as the reaction product of the constituents named in the formulas. One could make up the bath directly, and then there is more latitude in choice of ingredients. For example, sodium hypochlorite may be used in place of calcium hypochlorite. The substitution cannot readily be made commercially in the solid powder form because sufficiently strong sodium hypochlorite is not commercially available in solid form. The calcium form of hypochlorite is merely a means to employ hypochlorite in a strong solid form which with other ingredients produces a stable composition. The alkali emulsifies or saponifies the grease and fat and readily cleans other dirt or food residues.

The invention has several aspects as set forth herein. The formulas may be changed considerably from the examples given as indicated by the scope of the appended claims.

We claim:

1. A corrosion-inhibiting alkaline composition for cleaning zinc, iron and tin ware in an aqueous solution thereof at from cold to boiling temperatures consisting by weight essentially of about 85% of water-soluble inorganic alkaline detergent, about 5% to 7.2% of a solid hypochlorite salt of a metal from the group consisting of alkali metals and alkali earth metals, and about 9% to 10% of zinc compound from the group consisting of water-soluble zinc salts, zinc oxide, zinc hydroxide and zinc carbonate.

2. A composition according to claim 1 in which the zinc compound is water-insoluble.

3. A composition according to claim 1 in which the hypochlorite salt is calcium hypochlorite.

4. A composition according to claim 1 in which the alkaline detergent material is a mixture of anhydrous sodium carbonate and trisodium phosphate monohydrate.

5. A composition according to claim 1 in which the part of the alkaline detergent to the extent of 15% to 20% by weight of the composition is a sodium silicate, whereby the composition forms a bath which also protects aluminum.

6. A corrosion-inhibiting composition for cleaning zinc, iron, tin and aluminum ware in an aqueous solution thereof at from cold to boiling temperatures consisting by weight essentially of from about 65% to 70% of water soluble inorganic alkaline detergent, from about 15% to 20% of sodium silicate, about 5% to 6% of calcium hypochlorite, and about 9% to 10% of a zinc compound from the group consisting of water-soluble zinc salts, zinc oxide, zinc hydroxide and zinc carbonate.

7. A corrosion-inhibiting mixture for addition to a water-soluble inorganic alkaline detergent to render a bath of such material non-corrosive on zinc, iron, and tin ware at from cold to boiling temperatures, which consists by weight of about 1 part of a hypochlorite salt of a metal from the group consisting of alkali metals and alkali earth metals, and about 2 parts of a zinc compound from the group consisting of water-soluble zinc salts, zinc oxide, zinc hydroxide and zinc carbonate.

8. The method of inhibiting the action of aqueous solutions of inorganic alkaline detergents upon zinc, iron and tin ware at temperatures from 80° C. to boiling which comprises adding to the detergent solution having by weight about 85 parts of alkaline detergent, an inhibiting mixture consisting of about 5 to 7.2 parts of a solid hypochlorite salt of a metal from the group consisting of alkali metals and alkali earth metals and about 9 to 10 parts of a zinc compound from the group consisting of water-soluble zinc salts, zinc oxide, zinc hydroxide and zinc carbonate.

9. The method of inhibiting the action of

aqueous solutions of inorganic alkaline detergents upon zinc, iron, tin and aluminum ware at temperatures from 80° C. to boiling which comprises adding to the detergent solution having about 60 to 70 parts by weight of inorganic alkaline detergent, an inhibiting mixture consisting of about 15 to 20 parts by weight of sodium silicate, about 5 to 7.2 parts by weight of a solid hypochlorite salt of a metal from the group consisting of alkali metals and alkaline earth metals, and about 9 to 10 parts by weight of a zinc compound from the group consisting of water-soluble zinc salts, zinc oxide, zinc hydroxide and zinc carbonate.

10. A corrosion inhibiting mixture for addition to a water-soluble inorganic alkaline detergent to render a bath of such material non-corrosive of zinc, iron and tin ware at from cold to boiling temperatures, which consists of about 2 to 3 parts by weight of a solid hypochlorite salt of a metal from the group consisting of alkali metals and alkali earth metals, and about 9 to 10 parts by weight of a water-insoluble zinc compound which is soluble to provide zinc ions in said bath.

11. A corrosion-inhibiting cleaning bath for zinc, iron and tin ware at from cold to boiling temperatures comprising an aqueous solution having from ½ to 8 ounces per gallon of the products resulting on dissolution in water of a mass initially represented by a composition comprising by weight essentially 85% of water-soluble inorganic alkaline detergent, available chlorine in hypochlorite form corresponding to 5% to 6% of high test calcium hypochlorite of 70% to 71% available chlorine, and 9% to 10% of zinc compound selected from the group consisting of water-soluble zinc salts, zinc oxide, zinc hydroxide and zinc carbonate.

12. A bath according to claim 11 which is also non-corrosive on aluminum in which the percentage by weight of alkaline detergent material includes from 15% to 20% by weight of sodium silicate.

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