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UNITED STATES PATENT OFFICE

2,618,606

DETERGENT COMPOSITIONS CONTAINING METAL DISCOLORATION INHIBITORS

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No Drawing. Application February 4, 1949, Serial No. 74,715

14 Claims. (Cl. 252—137)

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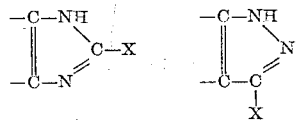
This invention relates to methods of inhibiting the discoloration of metals by certain inorganic salts and to improved compositions containing such salts and certain discoloration inhibitors.

Some inorganic salts, in aqueous solution, have the undesirable property of causing discoloration of various metals and alloys, such for example as copper, brass, German silver and the like. These salts are frequently present as constituents of detergent compositions, although some of them are also used alone for cleaning, water-softening or other purposes. The type of discoloration which they cause varies somewhat from metal to metal. It frequently manifests itself as a tarnished appearance upon kitchen ware, cutlery and household utensils, resulting from dishwashing or from prolonged soaking in solutions containing the salts. It appears in general when susceptible metals are exposed under sufficiently drastic conditions of time, temperature and concentration to aqueous systems containing alkali metal chlorides, sulfates or calcium-sequestering phosphates, the sodium and potassium salts being the most common of these. By "calcium-sequestering phosphates" I mean water-soluble salts of phosphoric acids which are poorer in water of constitution than orthophosphoric acid, such as tetrasodium pyrophosphate, pentasodium triphosphate (sometimes referred to as tripolyphosphate), "hexasodium tetraphosphate," and "hexasodium hexametaphosphate," as well as the various corresponding acid salts, such as disodium dihydrogen pyrophosphate, or the products of adding small amounts of free acid to the completely neutralized salts. These salts are capable of repressing calcium ions in aqueous solutions. I place "hexasodium tetraphosphate" and "hexasodium hexametaphosphate" in quotation marks to indicate that the salts so designated may be mixtures rather than pure chemical compounds. The "tetraphosphate" to which I refer is that compound or mixture which is described in U. S. Patent 2,031,827, and the "hexametaphosphate" is the glassy variety sometimes called Graham's salt which is described in U. S. Patent 1,956,515.

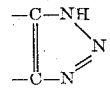
It is an object of this invention to provide means whereby such discoloration of metals may be minimized or prevented. Another object is to provide salt-containing compositions which have little or no tendency to cause discloration of surfaces of copper, brass, German silver or like susceptible metals. Another object is to provide detergent compositions which do not produce such discoloration. Other objects will appear in the description which follows.

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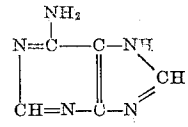
I have found that the objectionable discoloration phenonmena which I have described may in large measure be eliminated by mixing with the inorganic salt or incorporating in the salt-containing detergent composition or by dissolving in the aqueous solutions thereof small amounts of discoloration inhibitors. These inhibitors are organic compounds having a nucleus selected from the group of nuclei of the formulae



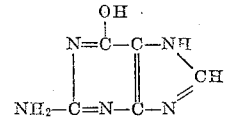
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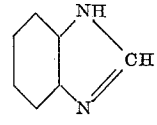
and tautomers thereof, wherein X may be hydrogen or an alkyl, aryl, aralkyl, alkylol or alkenyl radical, the free valence bonds in said nucleus being satisfied by hydrogen or by alkyl, aryl, aralkyl, alkylol or alkenyl radicals or by bivalent sulfonate-free organic residue. The following examples will make clear the type of compounds which I have found to be effective as discoloration inhibitors.



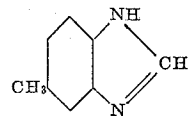
Adenine



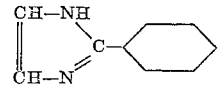
Guanine



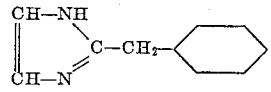
Benzimidazole



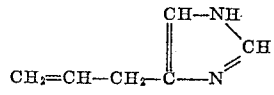
5-methyl benzimidazole



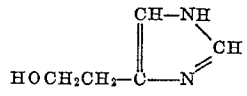
2-phenyl imidazole



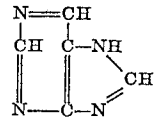
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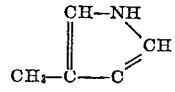
4-allyl imidazole



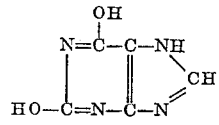
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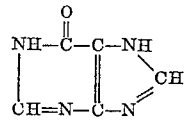
Purine



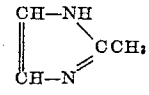
4-methyl imidazole



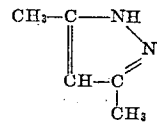
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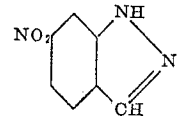
Hypoxanthine



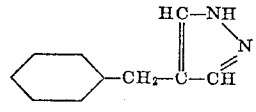
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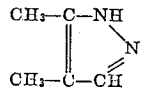
3,5-dimethyl pyrazole



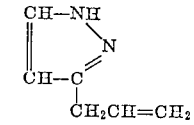
6-nitroindazole



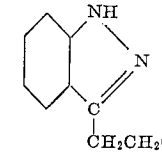
4-benzyl pyrazole



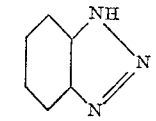
4,5-dimethyl pyrazole



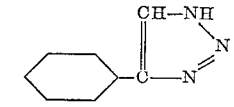
3-allyl pyrazole



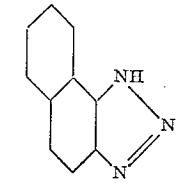
3-(β-hydroxyethyl) indazole



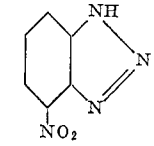
Benzotriazole



4-phenyl-1,2,3-triazole



1,2-naphthotriazole



4-nitrobenzotriazole

It will be perceived from these examples that my group of inhibitors includes a wide variety of compounds, since not only is variation possible in the members of the ring structure and their positions and bonding, but also a wide variety of substituents may be attached to the structures disclosed. The discoloration-inhibitive properties of the compounds are inherent in the recited structures however and persist (within the limitations discussed hereinafter) irrespective of the nature of the remainder of the molecule.

Some of the illustrative compounds are subject to sulfonation or sulfation (the term "sulfonate" being used generically herein to designate the product of either of these reactions), thereby combining within themselves structures which both promote and inhibit metal discoloration, and such products I do not claim as discoloration inhibitors.

In order to be effective, these inhibitors must be water-soluble, but the solubility need not be higher than is required to produce inhibiting action at the particular temperature in question. In general, solubility decreases with increasing molecular weight, and while compounds of the specified structure having molecular weight above 250 are in some cases effective, I find that most inhibitors which are useful in practical applications are of molecular weight less than 250.

Many inhibitors of my invention also vary in efficiency at different temperatures for reasons which appear not to be attributable to solubility

relationships. In such cases excellent results can be obtained by mixing the inhibitors. For example, good inhibition over a wide range of temperatures may be obtained by mixing an inhibitor which is most efficient at low temperature with one which is most efficient at high temperature.

The effectiveness and the water-solubility of the inhibitors may be affected by the pH of the solution. Some of them may be more effective, others less effective, at a high pH such as 10 or 11 than at a lower pH. By mixing inhibitors which are most effective at high pH with ones which are most effective at low pH, I obtain good protection over a wide range of pH values.

Partly because of considerations such as the above relative to solubility, temperature and pH, partly because of innate differences in efficiency among the inhibitors themselves, and partly also because of differences in the nature of the metal and of the discoloring agent, the quantity of inhibitor required for effective action differs from case to case. In all cases the quantity required is small, 0.01 per cent by weight of the aqueous system against which the metal is to be protected being ample. Because in some cases the effectiveness of discoloration inhibitors decreases when an optimum concentration is exceeded, I prefer in general to avoid using excessive amounts of inhibitor, such as would give concentrations higher than 0.01 per cent by weight in the aqueous system.

When these inhibitors are pre-mixed with an alkali metal chloride, sulfate or calcium-sequestering phosphate or with detergent compositions containing one or more of these salts, 1 percent by weight of the salt or the detergent compositions in the solution is sufficient in order to be effective in ordinary applications of such compositions. For example, calcium-sequestering phosphates, which are used for detergent or water-softening or water-treating purposes, are seldom present in an amount exceeding 1 percent by weight of the aqueous system, and this is also true of detergent compositions comprising these phosphates or alkali metal chlorides or sulfates. It will thus be seen that in order to have a salt-containing composition relatively free from objectionable discoloring action on metals, 1 percent inhibitor in said composition is ample.

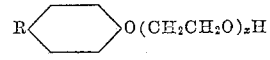
While the inorganic salts which I have mentioned are sometimes used alone in aqueous solution and thus come into contact with and discolor metals, it is more common to find them as constituents of compositions comprising surface-active synthetic detergents or wetting agents some of which do not, in the absence of such salts, cause discoloration. Among such surface-active agents may be mentioned non-ionic synthetics which possess marked detergent power such as high molecular ethers or esters of polyalkylene glycols or polyglycerols, and likewise thioethers, amines or amides which are derived from such polyglycols or polyglycerols. Such compounds are characterized by a molecular structure which is both lipophilic and hydrophilic, the lipophilic portion thereof normally containing a hydrocarbon chain or chains of high molecular weight, e. g. of about 8 to about 30 carbon atoms. Examples of such non-ionic surface active agents are alkyl and alkyl phenol ethers of polyethylene glycol, as well as sterol ethers and the corresponding thioethers, and likewise polyethylene glycol esters of fatty acids or other high molecular monocarboxylic acids. Other examples are the corresponding ethers and esters of polypropylene glycol, polybutylene glycol or polyglycerol, and the polyalkylene glycol ethers of partially esterified glycol, glycerol, sorbitol or mannitol or various partially anhydrized derivatives thereof. Other examples are compounds derived by reaction of 1,3-dioxolane with organic acids, anhydrides, esters, ethers, alcohols and amides of high molecular weight, by which reaction these compounds are rendered water-soluble and surface-active by the introduction of

$$(—OCH_2OCH_2CH_2—)$$

groups into their structure in accordance with U. S. Patent 2,395,971.

More specific examples of non-ionic surface active agents which have marked detergent power are compounds of the formulae:

$$RO(CH_2CH_2O)_xH$$



$$RS(CH_2CH_2O)_xH$$

$$RCOO(CH_2CH_2O)_xH$$

$$RNH(CH_2CH_2O)_xH$$

$$RCONH(CH_2CH_2O_xH$$

In the above formulae, R represents alkyl groups of about 8 to about 20 carbon atoms and x is an integer not less than 6 nor more than 20.

Valuable detergent properties are possessed by compositions containing 10 percent or more by weight of non-ionic surface-active agents possessing marked detergent power and 1 percent or more by weight of inorganic salts of the type specified, preferably a calcium-sequestering phosphate such as sodium triphosphate or sodium pyrophosphate. The remaining portion of the compositions is irrelevant to the matter of discoloration of metal; it may, for example, be inert material such for example as water, starch, urea, etc. My inhibitors find especially useful applications in protecting metals against discoloration by such compositions.

It will be perceived that the inhibitors are useful in a wide variety of compositions varying widely in constituents and in the relative proportions thereof. In general, the presence in such compositions of from 1 percent to 100 percent by weight of the specified alkali metal chlorides, sulfates or calcium-sequestering phosphates or mixtures thereof makes them discoloration agents, and their discoloration effect can be greatly reduced or eliminated by incorporating therein a sufficient amount, not exceeding 1 percent by weight thereof, of one or more of my inhibitors.

The inhibitors which I have described differ among themselves in efficiency and they also vary in effectiveness from metal to metal. In general, however, they are particularly useful in protecting certain easily discolored metals containing copper, such as copper itself and copper-containing alloys such as brass and German silver which I shall refer to as non-ferrous, coppery metals, as well as articles of such metals which are plated with imperfect or worn coatings of non-discoloring metals such as nickel or chromium.

The following examples, in which all parts are by weight, illustrate the action of the discoloration inhibitors, but it is to be understood that the examples are illustrative only and that the inven-

tion is not limited thereby but only by the terms of the appended claims.

Example 1.—Strips of German silver, brass and copper were hung in a 0.5% solution of pentasodium triphosphate in distilled water at 120° F. In each case, marked discoloration of the metal surface occurred within 3 hours. In duplicate tests wherein 0.5% benzotriazole had been added to the triphosphate (i. e. with 0.0025% benzotriazole in the solution) noticeably less discoloration took place.

Similar protection was afforded when the benzotriazole of Example 1 was replaced by 5-methyl benzimidazole.

Example 2.—This example was identical with Example 1 except that the triphosphate of Example 1 was replaced with tetrasodium pyrophosphate. Bad discoloration occurred in the absence of inhibitor, while noticeably less discoloration occurred in the presence of benzotriazole.

Example 3.—Strips of German silver and of brass were hung in a 0.5% solution of detergent mixture containing 4 parts of pentasodium triphosphate and 1 part of a commercial alkyl phenol ether of polyethylene glycol. After 3 hours at 120° F., all strips were badly discolored. In corresponding tests wherein 0.5% benzotriazole was added to the detergent mixture (i. e. with 0.0025% benzotriazole in the solution) noticeably less discoloration took place.

Similar results were obtained when tetrasodium pyrophosphate replaced the triphosphate of Example 3.

Similar protection was also afforded when 5-methyl benzimidazole replaced the benzotriazole of Example 3.

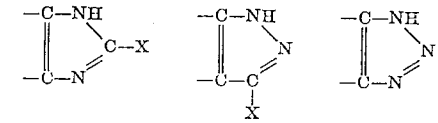
Protective action qualitatively similar to that described for benzotriazole is also obtained when 3,5-dimethyl pyrazole or 6-nitroindazole or adenine or guanine or benzimidazole or xanthine or 4-methyl imidazole or hypoxanthine or 1,2-naphthotriazole or 4-nitrobenzotriazole is used in place of benzotriazole in the above examples.

This invention is not limited to any particular physical form of the salt-containing compositions in which the inhibitor is incorporated. It is in general convenient to prepare mixtures of inorganic salts and inhibitors in solid form, such as granules or powders, or to mix them with other solids in granule or powder forms if desired. The non-ionic detergents are commonly liquids and if considerable quantities of them are present, special precautions are required if they are to be obtained as solids or powders. It is often more convenient to add water to compositions comprising inorganic salts, non-ionic detergents and inhibitor, thereby obtaining liquids which can be handled easily. Such liquids are desirable, for example, as dishwashing compounds.

This application is a continuation-in-part of my application Serial No. 790,720, filed December 9, 1947, and is related to my copending application Serial No. 74,713 of even date herewith.

Having thus described my invention, what I claim and desire to secure by Letters Patent is:

1. As a new composition of matter, a mixture consisting essentially of (*a*) a salt selected from the group consisting of sodium and potassium chlorides, sulfates, calcium-sequestering phosphates and mixtures thereof, and (*b*) a discoloration inhibitor for non-ferrous, coppery metals which is a water-soluble organic compound of molecular weight not exceeding 250 having a nucleus selected from the group consisting of nuclei of the formulae



and tautomers thereof wherein X is a member of the group consisting of hydrogen and alkyl, aryl, aralkyl, alkylol and alkenyl radicals, free valence bonds in said nucleus being satisfied by members of the group consisting of alkyl, aryl, aralkyl, alkylol or alkenyl radicals, bivalent sulfonate-free organic residues, and hydrogen, the inhibitor being present in an amount not exceeding 1 per cent by weight of the total composition and sufficient to inhibit discoloration of said metals when in contact with water and said detergent composition.

2. The composition of claim 1 wherein the inhibitor is adenine.

3. The composition of claim 1 wherein the inhibitor is 3,5-dimethyl pyrazole.

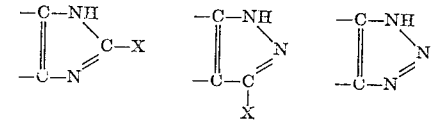
4. The composition of claim 1 wherein the inhibitor is benzotriazole.

5. The composition of claim 1 wherein the salt is sodium pyrophosphate.

6. The composition of claim 1 wherein the salt is sodium triphosphate.

7. The composition of claim 1 wherein the salt is sodium hexametaphosphate.

8. A detergent composition consisting essentially of (*a*) at least 10 per cent and not more than about 98 per cent by weight of a non-ionic surface-active agent having in its molecular structure a high molecular lipophilic group of from about 8 to 30 carbon atoms and possessing marked detergent power, (*b*) at least 1 per cent and not more than about 88 per cent by weight of salt selected from the group consisting of sodium and potassium chlorides, sulfates, calcium-sequestering phosphates and mixtures thereof, and (*c*) a discoloration inhibitor for non-ferrous coppery metals which is a water-soluble organic compound of molecular weight not exceeding 250 having a nucleus selected from the group consisting of nuclei of the formulae



and tautomers thereof wherein X is a member of the group consisting of hydrogen and alkyl, aryl, aralkyl, alkylol and alkenyl radicals, free valence bonds in said nucleus being satisfied by members of the group consisting of alkyl, aryl, aralkyl, alkylol or alkenyl radicals, bivalent sulfonate-free organic residues, and hydrogen, the inhibitor being present in an amount not exceeding 1 per cent by weight of the total composition and sufficient to inhibit discoloration of said metals when in contact with water and said detergent composition.

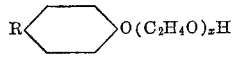
9. The composition of claim 8 wherein the non-ionic surface-active agent possessing marked detergent power is a high molecular ether of a polyethylene glycol.

10. The composition of claim 8 wherein the non-ionic surface-active agent possessing marked detergent power is a high molecular thioether of a polyethylene glycol.

11. The composition of claim 8 wherein the non-ionic surface-active agent possessing marked

detergent power is a high molecular ester of a polyethylene glycol.

12. The composition of claim 8 wherein the non-ionic surface-active agent possessing marked detergent power is an ether of the formula



wherein R is an alkyl group of about 8 to 20 carbon atoms and x is an integer not less than 6 nor more than 20.

13. The composition of claim 8 wherein the non-ionic surface-active agent possessing marked detergent power is a thioether of the formula

$$RS(C_2H_4O)_xH$$

wherein R is an alkyl group of about 8 to 20 carbon atoms and x is an integer not less than 6 nor more than 20.

14. The composition of claim 8 wherein the non-ionic surface-active agent possessing marked detergent power is an ester of the formula

$$RCOO(C_2H_4O)_xH$$

wherein R is an alkyl group of about 8 to 20 carbon atoms and x is an integer not less than 6 nor more than 20.

JOHN R. SCHAEFFER.

REFERENCES CITED

The following references are of record in the file of this patent:

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2,466,517	Blair	Apr. 5, 1949