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2,618,605

DETERGENT COMPOSITIONS CONTAINING METAL DISCOLORATION INHIBITORS

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17 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 suppressing 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 discoloration 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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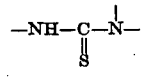
I have found that the objectionable discoloration phenomena which I have described may in large measure be eliminated by mixing with the inorganic salt or incorporating in the salt-containing detergent composition or by dissolving in the aqueous solutions thereof small amounts of discoloration inhibitors. These inhibitors are compounds which possess a single heterocyclic ring structure of not less than 5 nor more than 6 members, the ring containing a linking nucleus which includes 3 members of the ring and which has one of the formulae:



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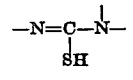

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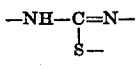

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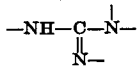

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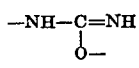
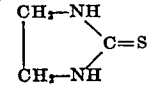
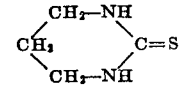


and the ring being completed by satisfying free valence bonds of any two atoms of said linking nucleus by a polyvalent sulfonate-free organic residue, the members of the ring exclusive of the linking nucleus being carbon and/or nitrogen atoms, and such free valence bonds as remain after completion of the ring being satisfied by an alkyl, aryl, alkylol, alkenyl or aralkyl radical or hydrogen.

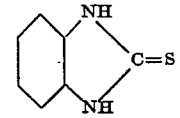
The following examples will make clear the type of compound which I have found to be effective as discoloration inhibitors:



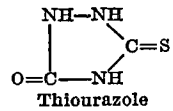
Ethylene thiourea



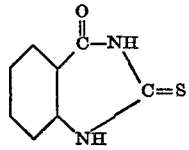
NN' trimethylene thiourea



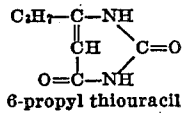
Phenylene thiourea



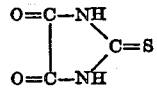
Thiourazole



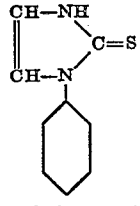
Benzoylene thiourea



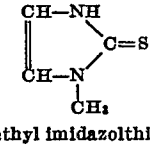
6-propyl thiouracil



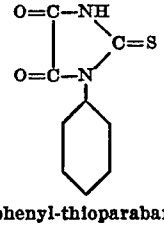
Thioparabanic acid



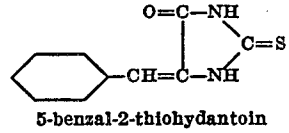
1-phenyl imidazolthione (2)



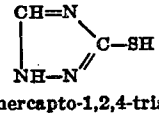
1-methyl imidazolthione (2)



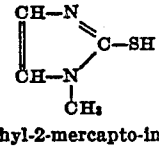
Monophenyl-thioparabanic acid



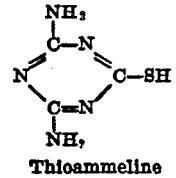
5-benzal-2-thiohydantoin



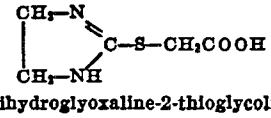
3-mercapto-1,2,4-triazole



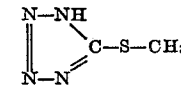
1-methyl-2-mercapto-imidazole



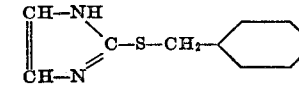
Thioammeline



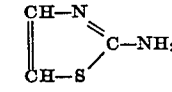
4,5-dihydroglyoxaline-2-thioglycolic acid



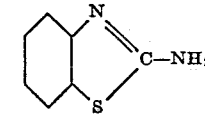
S-methyl-mercaptotetrazole



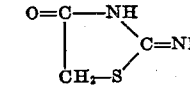
2-(benzylmercapto)-imidazole



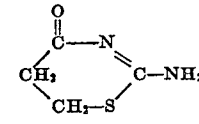
2-aminothiazole



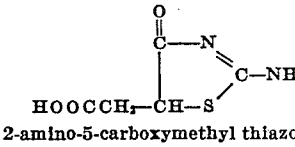
2-aminobenzothiazole



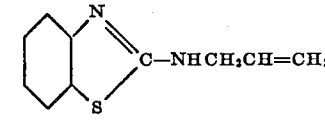
Pseudothiohydantoin



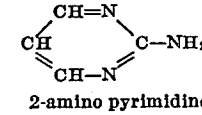
2-amino-4-ketodihydrothiazine



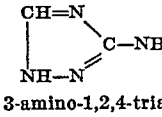
2-amino-5-carboxymethyl thiazolone



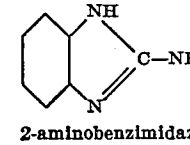
2-(allylamino)-benzothiazole



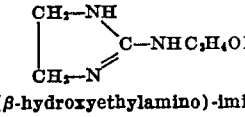
2-amino pyrimidine



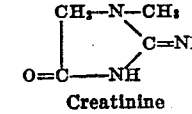
3-amino-1,2,4-triazole



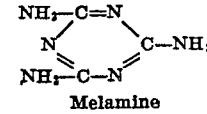
2-aminobenzimidazole



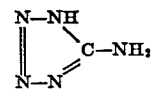
2-(β-hydroxyethylamino)-imidazoline



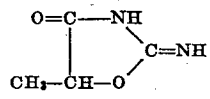
Creatinine



Melamine



5-amino-tetrazole



5-methyl-pseudohydantoin

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, for example, are more effective at a high pH such as 10 or 11 than at a lower pH, while others of them are not stable in strongly alkaline solution and are less effective at the higher 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.

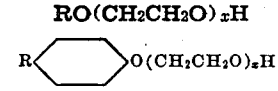
Partly because of considerations such as the above relative to solubility, temperature and pH, partly because of innate differences in efficiency among the inhibitors themselves, and partly also because of differences in the nature of the metal and of the discoloring agent, the quantity of inhibitor 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. I have in some cases observed that when the concentration of inhibitor exceeds an optimum value, efficiency decreases, and I therefore 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 per cent by weight of the salt or the detergent composition 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 per cent 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 if the inhibitor is not more than 1 per cent by weight of the salt-containing composition, its concentration in the aqueous solution will not be more than 0.01 per cent, and this concentration rarely exceeds the concentration at which any of my inhibitors begin to decrease in efficiency.

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 thio-ethers, 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 per cent or more by weight of non-ionic surface-active agents possessing marked detergent power and 1 per cent 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 per cent to 100 per cent by weight of the specified alkali metal chlorides, sulfates or calcium-sequestering phosphates or mixtures thereof make them discoloration agents, and their discoloration effect can be greatly reduced or eliminated by incorporating therein a sufficient amount, not exceeding 1 per cent 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 invention is not limited thereby but only by the terms of the appended claims.

EXAMPLE 1.—Strips of German silver (18% nickel, 17% zinc and 65% copper) were partially submerged in a 0.5% solution of pentasodium triphosphate in distilled water at 120° F. In each case a colored tarnish film soon appeared, golden at first and becoming dark blue or purple in about three hours. In duplicate tests with pentasodium triphosphate containing 0.5% ethylene thiourea (i. e. 0.0025% ethylene thiourea in the solution), noticeably less discoloration was produced.

EXAMPLE 2.—Strips of German silver and of brass were partially submerged in a 0.5% solution of tetrasodium pyrophosphate in distilled water at 120° F. In each case a colored tarnish film soon appeared, golden at first and becoming dark blue or purple in about 3 hours. In duplicate tests with tetrasodium pyrophosphate containing 1.0% ethylene thiourea (i. e. 0.005% ethylene thiourea in the solution) noticeably less discoloration occurred in 3 hours.

EXAMPLE 3.—A solution was prepared containing 0.5% of a detergent mixture of 4 parts of pentasodium triphosphate and 1 part of a commercial alkyl phenol ether of polyethylene glycol. Strips of German silver and of brass were immersed therein for 3 hours at 120° F. and became badly discolored. In corresponding tests wherein 0.5% ethylene thiourea was added to the detergent mixture (i. e. with 0.0025% ethylene thiourea in the solution), noticeably less discoloration appeared.

EXAMPLE 4.—A solution was prepared containing 0.5% of a detergent mixture of 4 parts of tetrasodium pyrophosphate and 1 part of a commercial alkyl phenol ether of polyethylene glycol. Strips of German silver were immersed therein as in Example 1, becoming badly discolored. In duplicate tests wherein 0.5% ethylene thiourea was added to the detergent mixture noticeably less discoloration appeared.

EXAMPLE 5.—A solution was prepared containing 0.75 part of a commercial alkyl phenol ether of polyethylene glycol and 0.25 part of sodium chloride in 100 parts of water. Strips of copper and of brass which were suspended in portions of this solution for 24 hours at 80° F. became darkened and discolored. Strips similarly treated with a like solution to which 0.05 part of ethylene thiourea had been added were only slightly changed in color.

EXAMPLE 6.—Strips of copper and of brass were suspended in 1% sodium chloride solutions at room temperature for 24 hours, during which time they became darkened and discolored. Strips similarly treated with a like solution to which 0.05 part of ethylene thiourea had been added were only slightly changed in color.

Ample protection is afforded when the proportion of ethylene thiourea is reduced to one tenth of the amount used in Examples 5 and 6.

Protective action qualitatively similar to that described for ethylene thiourea is also obtained when 2-amino-benzothiazole or 3-amino-1,2,4-triazole or NN'-trimethylene thiourea or 5-methyl-pseudohydantoin or phenylenethiourea or melamine or thiourazole or S-methyl mercapto-tetrazole or 6-propyl thiouracil or benzoylene thiourea or 3-mercapto-1,2,4-tetrazole or 2-amino-benzimidazole or creatinine is used in place of ethylene thiourea in Examples 1, 2 and 3.

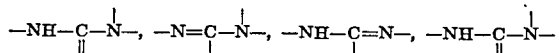
This invention is not limited to any particular physical form of the salt-containing compositions in which the inhibitor is incorporated. It is in general convenient to prepare mixtures of inorganic salts and inhibitors in solid form, as granules or powders, or to mix them with other solids in granule 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. For this reason it is often more convenient to add water to compositions comprising inorgnanic salts, non-ionic detergents and inhibitor, thereby obtaining liquids which can be handled easily. Such liquids, for example, are desirable as household dishwashing compounds.

This application is a continuation in part of my application Serial Number 790,720, filed December 9, 1947, now abandoned, and is related to my copending application Serial Number 74,712 of even date.

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 and is characterized by a single heterocyclic ring of not less than 5 nor more than 6 members, said ring containing a linking nucleus which includes 3 members of said ring and is selected from the group consisting of nuclei of the formulae



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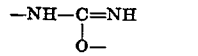
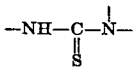


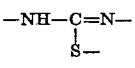
and said ring being completed by satisfying free valence bonds of any two atoms of said linking nucleus by a polyvalent sulfonate-free organic residue, the members of said ring exclusive of said linking nucleus being selected from the group consisting of carbon and nitrogen, such free valence bonds as remain after completion of the ring being satisfied by a member of the group consisting of alkyl, aryl, aralkyl, alkylol and alkenyl radicals and hydrogen, said inhibtor 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 composition.

2. The composition of claim 1 wherein the heterocyclic ring of the inhibitor is 5-membered and contains a linking nucleus of the formula



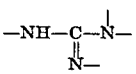
3. The composition of claim 1 wherein the inhibitor is ethylene thiourea.

4. The composition of claim 1 wherein the heterocyclic ring of the inhibitor is 5-membered and contains a linking nucleus of the formula



5. The composition of claim 1 wherein the inhibitor is 2-aminobenzothiazole.

6. The composition of claim 1 wherein the heterocyclic ring of the inhibitor is 5-membered and contains a linking nucleus of the formula



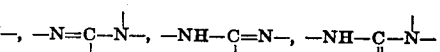
7. The composition of claim 1 wherein the inhibitor is 3-amino-1,2,4-triazole.

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

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

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

11. 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 and is characterized by a single heterocyclic ring of not less than 5 nor more than 6 members, said ring containing a linking nucleus which includes 3 members of said ring and is selected from the group consisting of nuclei of the formulae



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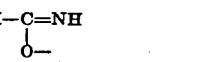


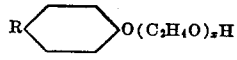
and said ring being completed by satisfying free valence bonds of any two atoms of said linking nucleus by a polyvalent sulfonate-free organic residue, the members of said ring exclusive of said linking nucleus being selected from the group consisting of carbon and nitrogen, such free valence bonds as remain after completion of the ring being satisfied by a member of the group consisting of alkyl, aryl, aralkyl, alkylol and alkenyl radicals and hydrogen, said 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 composition.

12. The composition of claim 11 wherein the non-ionic surface-active agent possessing marked detergent power is a high molecular ether of a polyethylene glycol.

13. The composition of claim 11 wherein the non-ionic surface-active agent possessing marked detergent power is a high molecular thioether of a polyethylene glycol.

14. The composition of claim 11 wherein the non-ionic surface-active agent possessing marked detergent power is a high molecular ester of a polyethylene glycol.

15. The composition of claim 11 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.

16. The composition of claim 11 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.

17. The composition of claim 11 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.

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