

UNITED STATES PATENT OFFICE

2,618,608

DETERGENT COMPOSITIONS CONTAINING
METAL DISCOLORATION INHIBITORSJohn R. Schaeffer, Wyoming, Ohio, assignor to
The Procter & Gamble Company, Ivorydale,
Ohio, a corporation of OhioNo Drawing. Application September 12, 1952,
Serial No. 309,383

10 Claims. (Cl. 252--137)

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This invention relates to methods of inhibiting the discoloration of metals by detergents and wetting agents and to improved compositions of this type containing discoloration inhibitors.

Some detergent compositions and wetting agents have the undesirable property of causing discoloration of various metals and alloys, such for example as copper, brass, German silver and the like. This effect may be noticed when the metallic surfaces are exposed to aqueous solutions of the composition, or when wet bars of the detergent lie thereon. The discoloration may manifest itself as a tarnished appearance upon kitchen ware, cutlery and household utensils resulting from dishwashing, for example. It is sometimes marked in soap dishes, constructed of these metals, which are exposed in bathroom or lavatory to the action of wet detergent bars. The surface layer of the bar also in some cases becomes discolored, and at times this discolored surface layer becomes detached from the bar and sticks to the metal surface.

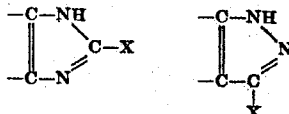
The discoloration phenomena which I have described appear in general when susceptible metals, under sufficiently drastic conditions of concentration, time and temperature, are exposed to aqueous systems containing the class of anionic synthetic detergents or wetting agents which may be described as high molecular organic sulfonation products which possess pronounced surface active properties. Discoloration of the metals is particularly intense when they are in contact with aqueous solutions of the various water soluble calcium sequestering phosphates, and with detergent and wetting compositions comprising mixtures of these phosphates with surface active organic sulfonation products. Long exposure of the metals to corresponding solutions containing other inorganic salts, such as chloride and sulfates, also produces discoloration to a minor extent, but in the detergent compositions herein claimed, i. e. those containing calcium-sequestering phosphates, the discoloration is rapid and particularly pronounced during detergent use.

It is an object of this invention to provide means whereby such discoloration of metals may be minimized or prevented. It is a further object to provide new detergent and wetting compositions which have little or no tendency to cause discoloration or surfaces of copper, brass, German silver and like susceptible metals. It is a further object to provide detergent compositions in bar form, which bars will not be subject to discoloration if kept in contact, while wet, with

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soap dishes or other surfaces of such metals. Other objects will appear in the description which follows.

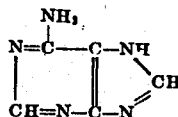
I have found that the objectionable discoloration phenomena which I have described may in large measure be eliminated by incorporating in the detergent or wetting composition or dissolving in the aqueous solutions thereof small amounts of certain discoloration inhibitors. These inhibitors are organic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



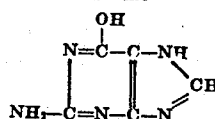
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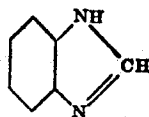
and tautomers thereof, wherein X may be hydrogen or an alkyl, aryl, aralkyl, alkylol or alkenyl radical, the free valence bonds in said nucleus being satisfied by hydrogen or by alkyl, aryl, aralkyl, alkylol or alkenyl radicals or by a bivalent sulfonate-free organic residue. The following examples will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



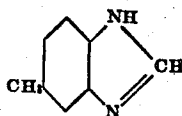
Adenine



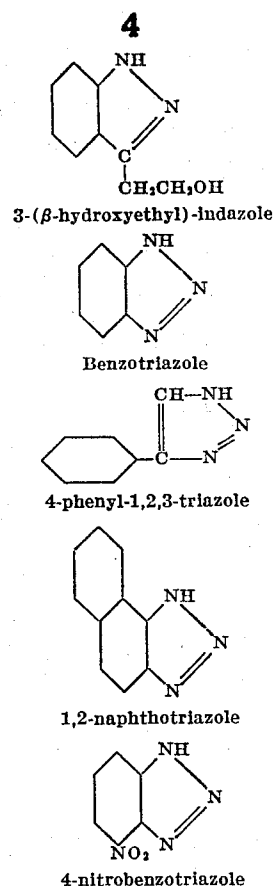
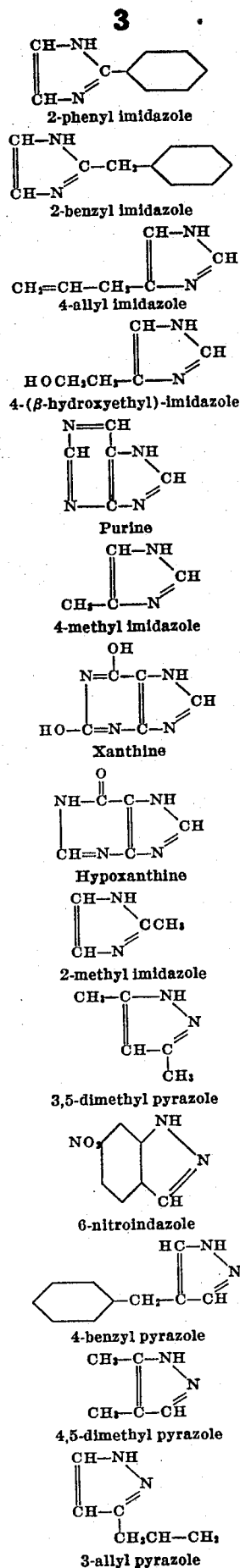
Guanine



Benzimidazole



5-methyl benzimidazole



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 may 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

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the inhibitors may be affected by the pH of the solution. Some of the inhibitors may be more effective, others less effective, at a high pH such as 10 or 11 than at a lower pH. By mixing ones which are most effective at high pH with ones which are most effective at low pH, good protection may be obtained 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 a discoloration inhibitor may decrease when an optimum concentration is exceeded, I prefer in general to avoid using amounts of inhibitor which would give concentrations higher than about 0.01 per cent by weight in the aqueous system.

While metal discoloration can be inhibited by adding the inhibitor to the water in which the surface active organic sulfonation product and calcium sequestering phosphates are to be dissolved, or to the pre-formed solution of these constituents, it is usually more convenient to premix the inhibitor with the sulfonation product and/or the phosphates in formulating the composition. This may be done in conventional manner and at any time, for example by mechanically mixing the constituents or by milling them in the presence of a little water. The invention is not limited as to the means or method of incorporating the inhibitor nor as to the stage in the process of manufacturing the composition at which the incorporation takes place nor as to the physical form of the resulting non-discoloring composition. If, for example, the finished product is to be an essentially dry detergent powder, flake or granule, the inhibitor may be incorporated and uniformly distributed in an aqueous paste containing the other ingredients and this paste may be spray-dried or roll-dried in conventional manner. In case milled detergent ribbons or bars are desired, the inhibitors may if desired be incorporated during the milling procedure. It will be understood that the composition containing the inhibitor may be in liquid, paste, powder, flake, bar or any other desired form.

The amount of inhibitor to be incorporated in the compositions of my invention should be sufficient to inhibit discoloration when the said compositions are used in the normal manner for the purpose for which they are intended. Thus experience has shown that when detergent compositions comprising high molecular organic sulfonated detergents and calcium-sequestering phosphates are used for laundering or dishwashing purposes (inorganic salts such as sodium chloride and sodium sulfate being frequently present in such compositions), or when such detergents or wetting agents are used in the textile industry, the concentration of such composition in the solution rarely exceeds 1 per cent by weight, even in extremely hard water. Furthermore, as was previously stated, the concentration of inhibitor required in the solution in order to be effective is usually less than 0.01 per cent by weight. In order therefore to have a detergent

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or wetting composition relatively free from objectionable discoloring action on metals, 1 per cent inhibitor in said compositions is ample.

In many cases 1 per cent inhibitor, based upon the total composition, is in excess of the amount necessary or desirable, in view inter alia of the cost of such inhibitors. For example, most such surface active organic sulfonated products in household use and many such detergents and wetting agents used in industry contain considerable quantities of inorganic salts and/or other materials and reduced quantities of sulfonated organic matter. In such cases I find that effective discoloration inhibition is often attained with amounts of inhibitor equivalent to about 3 per cent or less by weight of the sulfonation product contained therein but not exceeding 1 per cent by weight of the total composition.

The surface active organic sulfonation product may be any of a number of different types, all of which are water-soluble salts which are characterized by having in their molecular structure a long chain lipophilic group of about 8 to about 24 carbon atoms and also either a sulfonic acid radical or a sulfuric acid ester radical or mixtures of such radicals, there being preferably only one such sulfonic acid or sulfuric acid ester radical per molecule.

Among such compounds are the water-soluble salts of the sulfuric reaction product of aliphatic monohydric alcohols of about 10 to about 24 carbon atoms, and especially the water-soluble salts of sulfuric acid esters of normal primary aliphatic alcohols of about 10 to about 18 carbon atoms, such as those derived by reduction of coconut oil, cohune kernel oil, coquito nut oil, murumuru nut oil, ucuhuba nut oil, ouricuri oil, palm kernel oil, babassu oil or other oils of the coconut oil group, a group of tropical nut oils more than half of the combined fatty acids of which are lauric and myristic. The sulfuric esters of high molecular alcohols from other oils, fats and waxes, of high molecular unsaturated aliphatic alcohols, of high molecular branched chain primary alcohols and of high molecular secondary alcohols may also be used in the compositions of my invention.

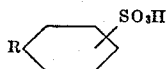
Other sulfuric esters which may be present in the compositions herein contemplated include water-soluble salts of sulfuric esters of polyhydric alcohols incompletely esterified with high molecular monocarboxylic acids such as soap-forming fatty acids, cyclic acids such as those of rosin and tall oil and naphthenic acids, and synthetic acids such as may be obtained by oxidizing paraffin hydrocarbons or petroleum or by hydrogenating carbon monoxide (sometimes referred to as the Fisher-Tropsch process) or by oxidizing the saturated or unsaturated hydrocarbons or oxygenated hydrocarbons resulting from this process. Specific examples of such detergents are the water-soluble salts of sulfuric esters of fatty acid monoglycerides and monoglycerolides, such as the sodium salt of the coconut oil fatty acid mono-ester of 1,2-dihydroxypropane-3-sulfuric acid ester, the sodium salt of the lauric acid ester of sulfated ethylene glycol, and the sodium salt of the oleic acid ester of sulfated diethylene glycol.

Similarly, water-soluble salts of ethers of high molecular normal primary alcohols and low molecular hydroxy alkyl sulfuric acid esters may be employed, such as the sodium salt of the coconut fatty alcohol mono-ether of glycerol monosul-

furic acid, and the sodium salt of lauryl ether of ethylene glycol sulfuric acid.

Similarly, water-soluble salts of sulfated higher fatty acid alkylolamides may be employed, such as the sodium salt of sulfated babassu oil fatty acid glycerol amide or of sulfated lauric amide of monoethanolamine.

Similarly, water-soluble salts of alkyl esters of sulfonated dicarboxylic acids, such as 2-ethyl hexyl ester of sodium sulfosuccinate, or water-soluble salts of high molecular fatty acid mono-esters of low molecular hydroxy alkyl sulfonic acids may be employed, such as the sodium salt of the palm kernel fatty acid mono-ester of 1,2-dihydroxy-propane-3-sulfonic acid, or the oleic acid ester of the sodium salt of isethionic acid. Likewise, water-soluble salts of high molecular fatty acid amides of low molecular amino alkyl sulfonic acids (for example, sodium salt of the oleic acid amide of N-methyl taurine), water-soluble salts of high molecular alcohol esters of sulfoarboxylic acids (for example, sodium salt of tetradecyl alcohol ester of sulfoacetic acid), water-soluble salts of low molecular sulfoarboxylic acid amides of alkylolamine esters of high molecular fatty acids (for example, sodium salt of the sulfoacetamide of amino ethyl laurate), water-soluble salts of high molecular alkyl aromatic sulfonic acids (for example, sodium alkyl naphthalene sulfonate or the sodium salt of the sulfonic acid derived by sulfonating the condensation product of benzene and a chlorinated kerosene fraction, such as represented by the formula



in which R represents alkyl groups of from about 9 to about 15 carbon atoms) and water-soluble salts of ethers of high molecular alcohols and low molecular hydroxy alkyl sulfonic acids (for example, monolauryl ether of 1,2-dihydroxy-propane-3-sodium sulfonate, and lauryl ether of the sodium salt of isethionic acid) may be employed.

The calcium sequestering phosphates have metal-discoloring properties when used in water even in the absence of sulfonated detergents or wetting agents, and they markedly contribute to any discoloration caused by the surface active sulfonated products herein referred to, when used in conjunction with them. Such contribution may assume importance when the amount of such calcium-sequestering phosphates exceeds about one per cent of the total weight of the composition. In view of the rapid and intense discoloration characteristics of detergent compositions containing calcium-sequestering phosphates, substantial amounts of chlorides and/or sulfates may be present in the composition without substantially accelerating the discoloration of the metal or substantially affecting the reduction in discoloration effected by the inhibitors of this invention. 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 aque-

ous 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.

The metal-discoloring compositions which are improved by adding my inhibitors may vary widely in the relative proportions of the constituents. Thus the surface active sulfonated products in admixture with 1 per cent or more of calcium sequestering phosphates mentioned above are active discolorants. Also mixtures containing only 1 or 2 per cent of the sulfonation product and phosphate, such as scouring powders or kitchen cleansers, sometimes cause trouble. In general, my inhibitors find practical application when used with detergent or wetting mixtures ranging in composition from 1 per cent to 99 per cent sulfonated detergent or wetting agent and from 1 per cent to 99 per cent calcium sequestering phosphate, and it will be understood that constituents other than these may also be present.

Thus the compositions of my invention consist essentially of a mixture of at least 1% and not more than 98% by weight of the water soluble detergent, at least 1% and not more than 98% by weight of calcium-sequestering phosphate, and a discoloration inhibitor in an amount not exceeding 1% by weight of the total composition and less than the amount of the water soluble detergent but sufficient to inhibit discoloration of non-ferrous coppery metals in contact with water and the composition.

The term "consisting essentially of" as used in the definition of the ingredients present in the composition claimed is intended to exclude the presence of other materials in such amounts as to interfere substantially with the properties and characteristics possessed by the composition set forth but to permit the presence of other materials in such amounts as not substantially to affect said properties and characteristics adversely.

These discoloration inhibitors appear to be 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 coatings or worn coatings of non-discoloring metals, such for example as nickel or chromium. It will be understood that various inhibiting compounds having the structures previously described may vary in effectiveness from metal to metal.

The following examples, in which all parts are by weight, illustrate the effectiveness of the discoloration inhibitors and ways in which I practice the invention, 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

80 parts of pentasodium triphosphate were mixed with 20 parts of sodium salt of the sulfuric acid mono-ester of the monoglyceride of coconut fatty acids. A 0.5% solution of this mixture was prepared in water, and sheets of German silver

(18% nickel, 17% zinc and 65% copper) were partially submerged therein for 3 hours at 120° F. A colored tarnish film soon appeared, golden at first and eventually becoming dark blue or purple. Similar sheets, similarly submerged in a 0.5% solution of a similar mixture to which 0.1 part of 5-methyl benzimidazole had been added developed only slightly tarnished appearance.

Very similar results were obtained when in place of the sulfated monoglyceride of the above example there was substituted:

(a) the sodium salt of a sulfonated alkyl benzene in which the alkyl group contained about 9 to about 15 carbon atoms, or

(b) the sodium salt of the sulfuric acid ester or normal primary alcohols of about 10 to about 18 carbon atoms, derived from coconut oil.

Very similar protective action is also shown when in place of the pentasodium triphosphate of the above examples there is substituted tetrasodium pyrophosphate or a glassy "hexasodium hexameta phosphate."

Example 2

A detergent composition was prepared containing approximately 54 parts of commercial triphosphate consisting of a mixture of a major proportion of pentasodium triphosphate and a minor proportion of tetrasodium pyrophosphate, 18 parts of the sodium salt of the sulfuric acid ester of coconut oil alcohols, 17 parts of sodium sulfate, and including small proportions of sodium carbonate, sodium chloride and other inorganic salts, and 8 parts of water.

Strips of brass and German silver as in Example 1 were suspended in a 0.5% solution of this mixture, becoming tarnished like those of Example 1 in the absence of a discoloration inhibitor. Strips similarly suspended in a like solution to which 0.05 part of benzotriazole (based on the weight of the detergent composition) had been added developed only slightly tarnished appearance.

Protective action in similar tests has been found for 0.02% 3,5-dimethyl pyrazole, 0.5% 6-nitroindazole or benzotriazole, 0.1% adenine, guanine, 5-methylbenzimidazole, or benzimidazole, 0.5% xanthine or 4-methyl imidazole, or 1.0% hypoxanthine, 1,2-naphthotriazole or 4-nitrobenzotriazole when added to detergent compositions such as that of Example 2.

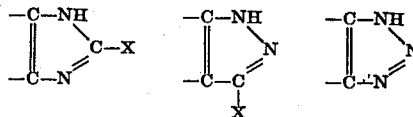
The composition of Example 2 is representative of commercial detergents comprising a mixture of water-soluble calcium-sequestering phosphates, sodium sulfate and/or chlorides, and high molecular organic sulfonation products which possess pronounced detergent power. Particularly efficient compositions of this character comprise a mixture of calcium-sequestering phosphates consisting predominantly (often about 75%) of pentasodium triphosphate but having a minor proportion (often about 25%) of tetrasodium pyrophosphate, a sodium alkyl sulfate in which the alkyl chain is that of a normal primary aliphatic alcohol of about 10 to about 18 carbon atoms, sodium sulfate in varying amount but commonly at least 10% by weight of the total, and a discoloration inhibitor, the ratio of the weight of the sulfonation product to the phosphates being about 1:1 to about 1:5, and the inhibitor being present in an amount not exceeding 1% by weight of the total composition, but sufficient to inhibit discoloration of metals when in contact with water and said composition.

This application is a continuation-in-part of

my application Serial No. 74,713, filed February 4, 1949.

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

1. A surface active composition consisting essentially of a mixture of at least 1 per cent and not more than 98 per cent by weight of a water-soluble detergent that is a salt of a high molecular organic sulfonation product of a material having in its molecular structure a long chain lipophilic group of from 8 to 24 carbon atoms; at least 1 per cent and not more than 98 per cent by weight of a calcium-sequestering phosphate and 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, said inhibitor being present in an amount not exceeding 1 per cent by weight of the total composition and less than the amount of said water-soluble detergent but sufficient to inhibit discoloration of said metals when in contact with water and said 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.

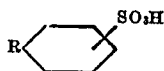
4. The composition of claim 1 wherein the inhibitor is benzotriazole.

5. The composition of claim 1 wherein the detergent is a water-soluble salt of the sulfuric reaction product of an aliphatic monohydric alcohol of about 10 to about 24 carbon atoms.

6. The composition of claim 1 wherein the detergent is a water-soluble salt of the sulfuric acid ester of primary straight chain aliphatic alcohols of about 10 to about 18 carbon atoms.

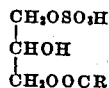
7. The composition of claim 1 wherein the detergent is a water-soluble salt of the sulfuric acid ester of alcohols derived from an oil of the coconut oil group.

8. The composition of claim 1 wherein the detergent is a water-soluble salt of a sulfonic acid of the formula



wherein R represents alkyl groups of about 9 to about 15 carbon atoms.

9. The composition of claim 1 wherein the detergent is a water-soluble salt of a sulfated monoglyceride of the formula



where RCO represents acyl groups of fatty acids of about 10 to about 18 carbon atoms.

10. The composition of claim 1 wherein the calcium-sequestering phosphate is a sodium salt.

JOHN R. SCHAEFFER.

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