INORGANIC PEROXY-COMPOUNDS CONTAINING ORGANIC ACTIVATORS

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3,130,165 Claims priority, application Great Britain Aug. 31, 1961 4 Claims. (Cl. 252-99)

The invention relates to detergent compositions containing oxygen-yielding compounds, such as sodium perborate, which provide a simultaneous washing and stain removing action.

Many detergent compositions contain an inorganic peroxo-compound, such as sodium perborate or sodium percarbonate, to provide bleaching and stain-removing properties. These compositions provide an excellent bleaching effect at the boil but at lower temperatures, for example 58–80°C, the bleaching action is slower. This means that the detergent composition can be used for washing “whites,” for example white cotton or linen goods such as table-linen, bed-linen and shirts, at the boil, with satisfactory stain removal. Such detergent compositions are also safe to use on coloured cotton goods and goods of more delicate fabrics such as those consisting of or containing rayon or artificial fibres, which are normally washed at lower temperatures, such as 50–80°C, without the risk of damage to the colour or the fabric. It is customary for housewives to use detergent compositions for boiling whites and then to wash, at a lower temperature, a second load of “coloureds” in the wash liquor previously used for washing the whites.

In domestic washing machines it is often impracticable or inconvenient to boil the wash liquor and it is desirable, therefore, to provide a detergent composition which has effective bleaching and stain removing properties at the temperatures conventionally used in domestic washing machines, viz. 50–80°C. At the same time, it is important that this low temperature bleaching effect should not be present when the second load of coloureds is washed, as it might have a deleterious effect on the colours.

Accordingly, it is an object of this invention to provide detergent compositions which have an accelerated bleaching effect on the first load of clothes washed and no accelerated bleaching effect on the second load of clothes washed in the same wash liquor as the first load.

It is a further object of this invention to provide a process for washing a load of white clothes and a load of coloured clothes in the same wash water whereby the white clothes are subjected to an accelerated bleaching effect and the coloured clothes are not subjected to said accelerated bleaching effect.

It has now been found that the customary inorganic peroxo-compounds, such as sodium perborate and sodium percarbonate, can be “activated” so as to have effective bleaching and stain-removing properties at washing machine temperatures (50–80°C) such “activation” being transient in nature and not persisting into the second load so that a second load of “coloureds” can be washed in the same wash liquor with no risk of damage to the colours. This is achieved by incorporating in a detergent composition containing such peroxo-compounds certain esters of phenols or substituted phenols.

The present invention provides a detergent composition comprising a soap and/or a synthetic detergent, an inorganic peroxo compound, and an ester of a phenol or substituted phenol with an alpha-chlorinated lower aliphatic carboxylic acid, such as chloracetic acid or alpha chloropropionic acid, the esters containing no ester group of any acid other than an alpha chlorinated lower aliphatic carboxylic acid. Permissible substituent groups on the phenol include carboxyl groups and sulphonic acid groups.

Preferred esters are:

- Chloracetyl phenol

\[ \text{CH}_2\text{COOCH}_2\text{Cl} \]

- Chloracetyl phenol-4-potasson sulphonate

\[ \text{CH}_2\text{OOC} \]

- Chloracetylphenol-3-carboxylic acid

\[ \text{CH}_2\text{CHCOOH} \]

- 3,4,5 tri(chloracetyl) gallic acid

\[ \text{CH}_2\text{OOC} \]

- Alpha chloropropionyl salicylic acid

\[ \text{CH}_2\text{COOC} \]

- Chloracetyl salicylic acid

\[ \text{CH}_2\text{COOH} \]

The last named ester is particularly preferred.

It is believed that the esters of the invention react with hydrogen peroxide in the washing solution (the hydrogen peroxide being provided by the inorganic peroxo compound) to produce a peryoxy chloroalkylphatic acid which is highly reactive and which provides an effective bleaching action, but that the peryoxy chloroalkylphatic acid is highly unstable so that the bleaching effect is transient and does not persist into the second load. In spite of this rapid loss of activity, the compositions of the invention do nevertheless give effective bleaching and stain removal on the first load.

The peroxo compounds of this invention are those having oxygen bleaching power. The customary inorganic peroxo-compounds are the alkali metal perborates, percarbonates and monopersulfates, such as sodium and potassium perborates and sodium and potassium percarbonates or complex salts such as KHSO₅-K₂SO₅-2KHSO₅.

The proportions of soap or synthetic detergent and of inorganic peroxo compound in the compositions can be those customarily used in conventional detergent bleaching compositions. For example, compositions containing 5 to 50%, by weight, of soap or synthetic detergent and 3 to 20%, by weight, of sodium perborate are suitable. The proportion of the ester in the compositions can vary from about 0.05 mole of ester per atom of available oxygen to about 2 moles of ester per atom of available oxygen. A proportion of one mole of ester per atom of available oxygen is highly effective.

Examples of suitable detergents include:

- Ordinary alkali metal soaps such as the sodium and potassium salts of the higher fatty acids of naturally occurring plant or animal esters (e.g., palm oil, coconut oil, babassu oil, soybean oil, castor oil, tallow, whale and fish oils, grease and lard, and mixtures thereof) or of synthetically produced fatty acids (e.g., by the oxidation of petroleum, or by hydrogenation of carbon monoxide by the Fischer-Tropsch process), of resin acid
(e.g. rosin and those resin acids in tall oil) and/or of naphthenic acids. Sodium and potassium soaps can be made by direct saponification of the fats and oils or by the neutralization of the free fatty acids which are prepared in a separate manufacturing process. These soaps are normally hydrogenated, at least slightly, for better keeping qualities.

(2) Synthetic organic detergents characterized by their high solubility in water, their resistance to precipitation by the constituents of hard water and their surface active and effective detergent properties, including:

(a) Synthetic detergents (true soaps): This class of synthetic detergents can be broadly described as the water-soluble salts, particularly the alkali metal salts, of organic sulfuric reaction product having in the molecular structure an alkyl radical containing from about 8 to about 22 carbon atoms and a radical selected from the group consisting of sulfonic acid and sulfuric acid ester radicals. Important examples of the synthetic detergents which form a part of the preferred compositions of the present invention are the sodium or potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols produced by reducing the glycerides of tallow or coconut oil with sodium or potassium alkyl benzene sulfonates, in which the alkyl group contains from about 9 to about 15 carbon atoms, especially those of the types described in United States Letters Patent Numbers 2,220,099 and 2,477,383; sodium alkyl glycol ether sulfonates, especially those ethers of the higher alcohols derived from coconut oil; sodium coconut oil fatty acid monoglyceride sulfates and sulfonates; sodium or potassium salts of sulfuric acid esters of the reaction product of one mole of a higher fatty acid (e.g., tallow or coconut oil alcohol) and about three moles of ethylene oxide, pentanol and/or potassium alkyl benzene sulfonates, which, in turn, contain about four units of ethylene oxide per molecule and in which the alkyl radicals contain about 9 carbon atoms; the reaction product of fatty acids esterified with isethionate and neutralized with sodium hydroxide where, for example, the fatty acids are derived from coconut oil; sodium or potassium salts of fatty acid amide of a methyl taurine in which the fatty acids, for example, are derived from coconut oil; and others known in the art, a number being specifically set forth in United States Letters Patent Numbers 2,486,921, 2,486,922 and 2,396,271.

(b) Nonionic synthetic detergents: This class of synthetic detergents may be broadly defined as compounds produced by the condensation of alkylene oxide groups (hydrophilic in nature) with an organic hydrophobic compound, which may be aliphatic or alkyl aromatic in nature. The length of the hydrophilic or poloxyalklyne radical which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements. For examples, a well known class of nonionic synthetic detergents is made available on the market under the trade name of "Pluronic." These compounds are formed by condensing ethylene oxide with an hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The hydrophobic portion of the molecule which, of course, exhibits water insolubility has a molecular weight of from about 1500 to 1800. The addition of poloxyethylene radicals to this hydrophobic portion tends to increase the water solubility of the molecule as a whole and the liquid character of the products is retained up to the point where poloxyethylene content is about 50% of the total weight of the condensation product.

Other suitable nonionic synthetic detergents include:

(i) The polyethylene oxide condensates of alkyl phenols, e.g., the condensation products of alkyl phenols having an alkyl group containing from about 6 to 12 carbon atoms in either a straight chain or branched chain configuration, with ethylene oxide, the said ethylene oxide being present in amounts equal to 10 to 25 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds may be derived from polymerized propylene, disobutylene, octane, or nonane, for example.

(ii) Those derived from the condensation of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylene diamine—products which may be varied in composition depending upon the balance between the hydrophilic and hydrophobic elements which is desired. For examples, compounds containing from about 40% to about 80% polyoxyethylene by weight and having a molecular weight of from about 5000 to about 11,000, resulting from the reaction of ethylene oxide groups with a hydrophobic base constituted of the reaction product of ethylene diamine and excess propylene oxide, said base having a molecular weight of the order of 2500 to 3000, are satisfactory.

(iii) The condensation product of aliphatic alcohols having from 8 to 18 carbon atoms, in either straight chain or branched chain configuration, with ethylene oxide, e.g., a coconut alcohol ethylene oxide condensate having from 10 to 30 moles of ethylene oxide per mole of coconut alcohol, the coconut alcohol fraction having from 10 to 14 carbon atoms.

(iv) Trialkyl phosphine oxides wherein one alkyl group ranges from 10 to 18 carbon atoms and two alkyl groups range from 6 to 12 carbon atoms; the alkyl groups can contain hydroxyl substituents; a specific example is tetra deyl dimethyl phosphine oxide.

(c) Zwitterionic detergents such as betaine and betaine-like detergents wherein the molecule contains both basic and acidic groups which form an inner salt giving the molecule both cationic and anionic hydrophilic groups over a broad range of wash water pH values. Some common examples of these detergents are described in U.S. Patents 2,082,275; 2,702,279; and 2,255,082.

(d) Amphoterically and ampholytic detergents which can be either cationic or anionic depending upon the pH of the system and which are represented by detergents such as dodecyl-beta-alanine, N-alkyltaurines such as the one prepared by reacting dodecylamine with sodium isethionate according to the teaching of U.S. 2,658,072, N-higher alkylationaric acids such as those produced according to the teaching of U.S. 2,438,091, and the products sold under the trade name "Miranol" and described in U.S. 2,528,378. The compositions can also contain conventional ingredients such as builder salts (e.g., pyrophosphates, tripolyphosphates, carbonates, acid pyrophosphates, phosphates, and silicates of alkali metals; nitro tricatic acid and ethylene diaminetetraacetic acid and alkali metal salts thereof; and sodium and potassium phytates); antiredeposition agents such as sodium carboxymethyl cellulose; soda builders such as ammonia amides, N-alkyl amides, and alkanolamides of fatty acids (e.g., coconut monooethanolamide and lauroyl and myristoyl glycerol amides, ethanol amides and isopropanol amides); optical bleaching agents; colour; and perfume. For heavy-duty laundering, the compositions of this invention preferably contain about 20% to about 60% sodium tripolyphosphate.

Example

A spray dried detergent composition was prepared, containing the following (all figures are parts by weight):

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Part</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium dodecyl benzene sulphate, the dodecyl</td>
<td>40</td>
</tr>
<tr>
<td>being derived from tetrapropylene</td>
<td>20</td>
</tr>
<tr>
<td>Sodium tripolyphosphate</td>
<td>35</td>
</tr>
<tr>
<td>Sodium silicate solids (ratio SiO₂:Na₂O=2:1)</td>
<td>5</td>
</tr>
<tr>
<td>Monoethanolamide of coconut fatty acids</td>
<td>2.5</td>
</tr>
<tr>
<td>Sodium carboxymethyl cellulose</td>
<td>1.0</td>
</tr>
<tr>
<td>Sodium sulphate</td>
<td>27.5</td>
</tr>
<tr>
<td>Moisture</td>
<td>10</td>
</tr>
</tbody>
</table>
80 parts by weight of this detergent powder were mixed with 8 parts by weight of sodium perborate and 12 parts by weight of chloracetyl salicylic acid.

A two-inch square piece of tea-stained cloth was washed for 5 minutes at 50° C. in a solution of 2.4 gms. of the above mixture in 400 ml. of distilled water. After rinsing in distilled water and drying and ironing the stain removal as measured on the Eel reflectometer was equivalent to an increase in reflectance of 30%.

A second two inch square piece of the same tea-stained cloth was then washed in the solution and rinsed, dried and ironed as described above. The stain removal was equivalent to an increase in reflectance of only 17%.

A test on wash liquor after the first piece of cloth had been washed and before the second piece has been added showed that it gave no titratable liberation of iodine when added to acidified potassium iodide. This indicates that the liquor no longer had any activated bleaching action.

In a similar experiment in which the chloracetyl salicylic acid was replaced by sodium sulphate the stain removal as measured on the Eel reflectometer was equivalent to an increase in reflectance of 16% on the first load and 16% on the second.

When, in the above example, equivalent amounts of chloracetyl phenol, chloracetyl phenol-4-potassium sulfonate, chloracetylphenol-2-carboxylic acid, 3,4,5-tri(chloracetyl) gallic acid, or alpha chloropropionyl salicylic acid are substituted for the chloracetyl salicylic acid, substantially equivalent results are obtained.

When, in the above example, equivalent amounts of sodium or potassium percarbonates and monopersulfates are substituted for the sodium perborate, substantially equivalent results are obtained.

Similarly, when other detergent materials are used containing sodium or potassium, coconut or tallow soap; the alkali metal, ammonium, and substituted ammonium salts of coconut or tallow alkyl sulfates; sodium coconut or tallow alkyl glyceryl ether sulfonates; and alkali metal salts of the sulfonic acid ester of the reaction product of one mole of coconut or tallow alcohols and three moles of ethylene oxide are substituted in equivalent amounts by weight for the sodium alkyl benzene sulfonate of this example, substantially equivalent results in improved bleaching activity are obtained. Also, the substitution of other builders such as alkali metal pyrophosphates, phosphates, phytates, etc., for the sodium tripolyphosphate, or the elimination of builders altogether does not affect the performance of the bleaching system.

Furthermore, the substitution of coconut fatty acid ammonia amide, isopropanol amide, or glycerol amide for the ethanol amide of this example, or the elimination of suds builders altogether does not affect the performance of the bleaching system.

What we claim is:

1. A household laundry detergent composition comprising (A) from 5 to 50% of an organic detergent selected from the group consisting of (1) alkali metal soaps of higher fatty acids, (2) anionic non-soap synthetic detergents, (3) nonionic synthetic detergents, (4) zwitterionic synthetic detergents, and (5) amphoteric synthetic detergents; (B) from 3-20% by weight of inorganic peroxy-compound selected from the group consisting of sodium and potassium perborates, percarbonates and monopersulfates; and (C) from about 0.5 to about 2.0 moles per mole of available oxygen in said peroxy-compound of an ester of a phenol selected from the group consisting of phenol and substituted phenols containing at least one substituent group selected from the group consisting of carboxyl groups and sulfonic acid groups and an alpha-chlorinated lower aliphatic acid selected from the group consisting of acetate and propionate acids.

2. The detergent composition of claim 1 in which the ester is selected from the group consisting of chloracetyl phenol; chloracetyl phenol-4-potassium sulfonate; chloracetyl phenol-3-carboxylic acid; 3,4,5-tri(chloracetyl) gallic acid; alpha chloropropionyl salicylic acid; and chloracetyl salicylic acid.

3. The detergent composition of claim 1 in which the ester is chloracetyl salicylic acid.

4. The detergent composition according to claim 1 wherein there is one mole of ester per atom of available oxygen.

References Cited in the file of this patent

UNITED STATES PATENTS
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3,003,910 Dithmar Oct. 10, 1961
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OTHER REFERENCES