PEROXIDE-ESTER BLEACHING PROCESS AND COMPOSITIONS


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18 Claims. (Cl. 8—111)

This invention relates to processes of bleaching and to bleaching compositions; in particular it relates to processes and to compositions suitable for removing stains from textile materials.

Many detergent compositions contain an inorganic per-salt such as sodium perborate or percarbonate to provide bleaching properties. These per-salts provide a satisfactory bleach when the detergent is used at the boil, but at lower temperatures their action is rather slow. This disadvantage is becoming important with the growing use of washing machines which operate at a temperature of, for example, 50–60 °C. It is an object of the present invention to provide a more effective bleach in the normal washing period at this temperature than is obtained with the per-salt alone.

Processes and compositions according to the invention also find application in the textile industry and in commercial laundering.

It has been found that improvements in bleaching can be obtained by the use of an aqueous solution containing hydrogen peroxide and an organic carboxylic ester, as characterized below.

It has further been found that improved bleaching compositions can be provided which contain an inorganic per-salt together with an organic carboxylic ester having one or more ester groupings in the molecule. The esters which are suitable for use according to the invention are characterized by the following per-acid formation test:

To a solution at 60 °C. containing the following in 1,000 ml. of distilled water:

- 2.5 gms. NaH2P04.10H2O
- 0.615 gms. NaB03.H2O.3H2O
- (at 10.4% available oxygen)
- 0.5 gms. sodium tetra propylene benzene sulphonate

is added an amount of ester, in equimolecular ratio to the available oxygen. Water-soluble esters and those which are liquid at 60 °C. are added direct to the aqueous solution; other esters should be dissolved in 10 ml. ethyl alcohol, before addition, the volume of distilled water being reduced in such cases to 990 ml. The mixture is mechanically stirred by means of a ½” glass stirrer at 600 revs. per minute and maintained at 60 °C. After 5 minutes a 100 ml. aliquot is withdrawn and immediately pipetted on to a mixture of 250 gms. of cracked ice and 15 ml. of glacial acetic acid. 0.4 gms. of potassium iodide is then added. The liberated iodine is immediately titrated with 0.1 N sodium thiosulphate, using starch as indicator, until the first disappearance of the blue color.

Esters which give a titre of 1.5 ml. or more in this per-acid formation test, may be used in bleaching compositions and processes according to the invention.

According to the present invention there is provided a bleaching process in which an aqueous solution of hydrogen peroxide and an organic carboxylic ester which gives a titre of not less than 1.5 ml. of 0.1 N Na2S2O3 in the per-acid formation test defined above, is used.

The present invention further provides a bleaching composition which contains an inorganic per-salt together with an organic carboxylic ester which gives a titre of not less than 1.5 ml. of 0.1 N Na2S2O3 in the per-acid formation test defined above.

Esters which give a titre of not less than 1.5 ml. 0.1 N Na2S2O3 in the test defined above and hence may be used according to the invention, include compounds within the class

\[
R_1-O-C-R_2
\]

where \( R_1 \), attached to the oxygen atom of the ester link, exerts an electron-attracting effect; and \( R_2 \) may be an alkyl, aryl or aliphatic radical or a substituted alkyl, aryl or aliphatic radical.

The esters should not yield easily oxidizable hydrolysis products such as polyhydric phenols, unsubstituted lower aliphatic aldehydes, and alpha and beta diketones.

Examples of esters within the scope of the invention, that is which give a titre of at least 1.5 ml. 0.1 N Na2S2O3 in the per-acid formation test defined above, are found in the following classes:

(a) Esters of phenols and substituted phenols—examples are:
- Phenyl acetate
- Phenyl benzoate
- Phenyl p-nitrobenzoate
- Phenyl cinnamate
- p-Cresyl acetate
- o-Nitro phenyl benzoate
- O-Phenyl phenyl benzoate
- p-Phenyl phenyl acetate
- Phenyl furoate
- p-Bromophenyl benzoate
- Benzoyl ester of commercial potassium (or sodium) phenol sulphonate
- Phenyl nicotinate

(b) Esters of monohydric aliphatic alcohols containing substituents which exert an electron-attracting influence, such as trichloroethyl—example is: Trichloroethyl acetate.

(c) Esters of polyhydric aliphatic alcohols containing several ester groups situated on adjacent carbon atoms, particularly:
- Mannitol hexa acetate
- Sorbitol hexa acetate

(d) Esters of mono- and disaccharides containing preferably 3 or more ester groups on adjacent carbon atoms—examples are:
- Fructose penta acetate
- Glucose penta acetate
- Glucose tetra acetate
- Sucrose octa acetate

(e) Esters containing 2 ester groups attached to the same carbon atom such as may be obtained by acylation of aldehydes—examples are:
- p-Nitrobenzaldehyde diacetate
- Glycolic aldehyde triacetate
- Benzaldehyde diacetate
- Furfural diacetate
- Chloral diacetate

(f) Esters of the enolic forms of ketones, preferably not alpha- and beta-diketones or other readily oxidizable ketones—examples are:
- Δ2-cyclohexenyl acetate
- Isopropenyl acetate
(g) Esters of N-substituted derivatives of hydroxylamine—an example is: Acetyl acetohydroxamic acid

Solid esters lend themselves readily to incorporation in compositions in solid form. Water-insoluble solid esters should, however, be in a finely-divided state in a solid composition.

Hydrogen peroxide cannot, of course, be included in a solid composition, and bleaching solutions prepared from hydrogen peroxide should be prepared as required for use.

The hydrogen peroxide may be added to the solution as such, or may be liberated in situ from a per-salt.

By "inorganic per-salt" is meant a salt which will give rise to hydrogen peroxide in aqueous solution. Suitable compounds are alkali metal perborates, percarbonates, perpyrophosphates and persilicates. These are not true per-salts in the strict chemical sense but are believed to contain hydrogen peroxide of crystallization, which is liberated in aqueous solution.

The invention can be applied to bleaching baths such as are used for treating textiles, to wash liquors, such as are used in commercial laundering and to solid bleaching compositions. Solid bleaching compositions may contain, in addition to a per-salt and an ester according to the invention, inert salts, alkaline agents and a small proportion of detergent. The invention may further be applied to detergent compositions, which will contain an organic detergent, which may be soap or an organic soapless detergent. Suitable organic soapless detergents are the alkyl aryl sulphonates, alkyl sulphates and the salts of esters or ethers of isethionic acid.

Compositions according to the invention should preferably contain one or more alkaline substances, in amounts such that similar compositions not containing esters would give a pH value within the range 9–11 when dissolved at the desired bleaching concentration. Most common detergent compositions contain alkaline material suitable for this purpose. Suitable alkaline materials are, for instance, soap, alkali metal carbonates, phosphates (including orthophosphates, and water-soluble condensed phosphates, such as triphosphates, and pyrophosphates) and silicates.

When the invention is applied to bleaching or wash liquors, alkali sufficient to give an initial pH of 9–11 is preferably present in the bleaching or wash liquor before addition of the ester.

Compositions according to the invention may contain any of the conventional adjuncts present in detergent compositions. There may be mentioned, supplementary builders, inert and organic materials such as alkali metal sulphates, chlorides, carboxy methyl cellulose and fluorescent agents.

Compositions according to the invention must not contain water in an amount sufficient to permit appreciable chemical reaction between the components prior to use.

The proportions of per-salt and ester which may be present in compositions according to the invention will depend on the time and temperature of bleaching, the degree of bleaching required, the concentration of the bleaching solution and the individual ester and per-salt used. Used most conditions, these proportions should be such as to give a per-salt concentration in solution equivalent to 0.001 to 1.0% available oxygen.

Having regard to these factors, bleaching effects may be obtained with compositions according to the invention containing widely varying ratios of per-salt to ester. It is convenient to measure the activity of the per-salt in terms of available oxygen. Generally, ratios of from 1/4 to 2 and particularly from 1/2 to 1½ molecules of ester per one atom of available oxygen are preferred. (In converting such ratios to ratios by weight, account must be taken of the molecular weight of the ester and the available oxygen content of the per-salt used.) In particular, it is preferred to use approximately chemically equivalent amounts of ester and per-salt. In determining such chemically equivalent amounts it should be realized that with esters containing more than one ester grouping, not all the ester groups will necessarily react with the available oxygen of the per-salt. Thus, with aldehyde diacetates, only one group is believed to react, with glucose tetracetate one group reacts and with glucose pentacetate two groups react.

When solutions are used which are obtained by adding hydrogen peroxide and an ester according to the invention to an alkaline bath, the preferred weight ratio is from 2 to 15 parts of ester to 1 part of hydrogen peroxide (100%) depending on the molecular weight of the ester used.

When compositions according to the invention are to be used primarily as a bleach, for instance, for addition to alkaline textile bleaching baths or wash liquors. Such compositions may contain any proportion of ester and per-salt, these components being preferably present in the ratio 1/4 to 2 molecules of ester per one atom of available oxygen, preferably 1/2 to 1½ molecules per one atom of available oxygen. Thus, by way of example, a composition may contain 33% per-salt having 10% available oxygen and 67% of the benzoyl ester of commercial sodium phenol sulphonate. Using per-salt having 15% available oxygen, the composition may contain 25% of the per-salt and 75% of the benzoyl ester of commercial sodium phenol sulphonate.

When an organic detergent is present in compositions according to the invention, improvements in bleaching can be obtained at normal washing concentrations. Thus, for example, using a detergent composition according to the invention at a concentration of 1% in aqueous solution, improvements may be obtained if amounts of as little as 1% of per-salt and 2% of ester by weight of the composition are present. In such compositions, however, the amount of per-salt taken should provide at least 0.1% available oxygen based on the composition. Generally, detergent compositions will contain from about 10 to about 50% by weight of organic detergent. The mixed ester/per-salt content may be as high as 70% by weight provided that these components are taken in ratios 1/4 to 2, preferably 1/2 to 1, molecules of ester per one atom of available oxygen. Effective proportions of ester and per-salt in detergent compositions will in general lie within the range from 2 to 30% of ester and 1 to 15% of per-salt by weight of the composition.

Best results in bleaching according to the invention are obtained under conditions of effective agitation such as exist, for instance, in a washing machine. The following examples illustrate the invention:

Example 1

A bleach bath at 60° C. was prepared containing the following ingredients:

0.5% tetradsodium pyrophosphate
0.021% hydrogen peroxide (as 100%) (H₂O₂)
0.136% chloral diacetate

the ingredients being added in the above order.

A length of cotton cloth was stained by immersion in boiling tea extract for one hour. It was then thoroughly rinsed, wet and cut into test-pieces whose percent reflectances were measured in a Hunter reflectometer using the blue-filter. The percent reflectance of the test pieces was measured again after bleaching. The bleach obtained was expressed as the difference in the two percent reflectance readings on each test-piece.

A piece of tea-stained cotton cloth was immersed in the bleach bath, at a cloth to liquor ratio of 1 to 20, and stirred for 15 minutes, the temperature being maintained at 60±2° C. After this time the cloth was rinsed three times, ironed and its percent reflectance measured. The increase in percent reflectance was 22.7. In a similar control experiment carried out in the absence of chloral...
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Example 2

A spray-dried detergent powder had the following percentage composition:

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium dodecyl (tetrapropylene) benzene sulphonate</td>
<td>21.9</td>
</tr>
<tr>
<td>Lauryl isopropanolamide</td>
<td>2.7</td>
</tr>
<tr>
<td>Tetrasodium pyrophosphate</td>
<td>19.7</td>
</tr>
<tr>
<td>Pentasodium tripolyphosphate</td>
<td>15.3</td>
</tr>
<tr>
<td>Alkaline sodium silicate (anhydrous)</td>
<td>5.5</td>
</tr>
<tr>
<td>Sodium carboxy methyl cellulose (60%)</td>
<td>1.6</td>
</tr>
<tr>
<td>Sodium sulphate</td>
<td>21.3</td>
</tr>
<tr>
<td>Moisture</td>
<td>12.0</td>
</tr>
</tbody>
</table>

To 77.3 parts of this detergent powder was added 10 parts of sodium perborate tetrahydrate and 12.7 parts of glucose penta-acetate and the whole was mixed.

An 0.5% solution of the finished composition was prepared at 60°C and a tea-stained cloth, prepared as described in Example 1, was then immersed and stirred for 15 minutes, the temperature being maintained at 60±2°C. The cloth was then rinsed three times, ironed and its percent reflectance measured. The increase in percent reflectance was 19.0. In a control experiment without glucose penta-acetate the increase in percent reflectance was only 13.2.

Example 3

To 76.4 parts of a soap powder containing:

<table>
<thead>
<tr>
<th>Percentage</th>
<th>Component</th>
</tr>
</thead>
<tbody>
<tr>
<td>30.4%</td>
<td>Sodium soap</td>
</tr>
<tr>
<td>16.0%</td>
<td>Sodium carbonate</td>
</tr>
<tr>
<td>2.8%</td>
<td>Anhydrous neutral sodium silicate</td>
</tr>
<tr>
<td>30.8%</td>
<td>Water</td>
</tr>
</tbody>
</table>

was added 8.0 parts of sodium perborate tetrahydrate and 15.6 parts of the benzoyl ester of commercial sodium phenol sulphonate and the whole was mixed. An 0.8% solution of the finished product was prepared at 60°C. To this solution was added a tea-stained cloth at a cloth to liquor ratio of 1 to 20 and stirred for 15 minutes, the temperature being maintained at 60±2°C. The cloth was then rinsed 3 times, ironed and its percent reflectance measured. The increase in percent reflectance was 20.0. In a control test in the absence of ester the increase in percent reflectance was only 14.3.

In the specified per-acid formation test, the esters used in the above examples gave the following:

<table>
<thead>
<tr>
<th>Ester</th>
<th>Titration (ml. 0.1 N sodium thiosulphate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloral dicinate</td>
<td>4.6</td>
</tr>
<tr>
<td>Gluconic acid</td>
<td>4.3</td>
</tr>
<tr>
<td>Benzoyl ester of commercial sodium phenol sulphonate</td>
<td>6.5</td>
</tr>
</tbody>
</table>

We claim:

1. A process of bleaching soiled textile materials comprising the steps of placing the article to be bleached in an aqueous solution of hydrogen peroxide and an organic carboxylic ester having a titre in the per-acid formation test of not less than 1.5 ml. 0.1 N Na,S,O₃, allowing the article to remain in the solution for a normal washing period and rinsing the article.

2. A process according to claim 1 in which an alkaline material sufficient to give an initial pH between 9 and 11 is present in the bleaching solution before addition of the ester.

3. A process according to claim 1 in which the ester is the benzoyl ester of commercial alkali metal phenol sulphonate.

4. A process of bleaching soiled textile materials comprising the steps of placing the article to be bleached in an aqueous solution of hydrogen peroxide and an organic carboxylic ester having a titre in the per-acid formation test of not less than 1.5 ml. 0.1 N Na,S,O₃, allowing the article to remain in the solution at a temperature substantially below the boiling point of the solution for a normal washing period and rinsing the article.

5. The process according to claim 1 in which the ester is a phenyl ester of a carboxylic acid.

6. A composition for use in bleaching soiled textile materials comprising an inorganic per-salt and an organic carboxylic ester which gives a titre in the per-acid formation test of not less than 1.5 ml. 0.1 N Na,S,O₃.

7. The composition according to claim 6 which includes an alkaline material in an amount sufficient to provide a pH of 9–11 when the composition is placed in an aqueous solution.

8. A composition for use in bleaching soiled textile materials in an aqueous bath comprising an inorganic per-salt, an organic detergent, and an organic carboxylic ester, said ester being one which gives a titre in the per-acid formation test of not less than 1.5 ml. 0.1 N Na,S,O₃.

9. The composition according to claim 6 wherein the ester is a phenyl ester of a carboxylic acid.

10. The composition according to claim 6 wherein the ester is an ester of a monohydric aliphatic alcohol.

11. The composition according to claim 6 wherein the ester is an ester of a polyhydric aliphatic alcohol containing several ester groups situated on adjacent carbon atoms.

12. The composition according to claim 6 wherein the ester is an ester of a saccharide containing several ester groups on adjacent carbon atoms.

13. The composition according to claim 6 wherein the ester is an ester containing two ester groups attached to the same carbon atom.

14. The composition according to claim 6 wherein the ester is an ester of the enolic form of a ketone.

15. A composition for use in bleaching soiled textile materials in an aqueous bath comprising a soapless detergent, an alkaline material sufficient to provide a pH of 9–11 when the composition is placed in the aqueous bath, an inorganic per-salt, and the benzoyl ester of commercial sodium phenol sulphonate.

16. A composition for use in bleaching soiled textile materials in an aqueous bath comprising a soapless detergent, an alkaline material sufficient to provide a pH of 9–11 when the composition is placed in the aqueous bath, from 1–15% by weight of the composition of the inorganic per-salt, and from 2–30% by weight of the composition of the benzoyl ester of commercial sodium phenol sulphonate.

17. The composition of claim 6 wherein the organic carboxylic ester and the inorganic per-salt are present in amounts sufficient to provide from ½ to 2 molecules of ester per one atom of available oxygen.

18. The composition of claim 8 wherein the organic carboxylic ester and inorganic per-salt are present in amounts sufficient to provide from ½ to 2 molecules of ester per one atom of available oxygen.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,955,905

October 11, 1960

Thomas Daniel Davies et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 61, for "Used" read -- Under --; column 6, line 75, list of references cited, under the heading, "FOREIGN PATENTS", for "Sept. 3, 1951" read -- Sept. 3, 1935 --.

Signed and sealed this 11th day of April 1961.

(SEAL)

Attest:
ERNEST W. SWIDER

Attesting Officer

ARTHUR W. CROCKER
Acting Commissioner of Patents
UNITED STATES PATENT OFFICE
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