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BLEACHING PROCESS AND COMPOSITION

Peter Roscoe Hartley Speakman, Gateshead on Tyne, and David Geoffrey Stewart, Newcastle Upon Tyne, England, assignor to The Procter & Gamble Company, Cincinnati, Ohio

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ABSTRACT OF THE DISCLOSURE

A bleaching process in which the bleaching agent is an aqueous solution containing a benzoyl glutaryl peroxide of the formula

$$RCO{\cdot}OO{\cdot}CO(CH_2)_3CO_2H$$

wherein R is phenyl or substituted phenyl is disclosed. Bleaching compositions containing such peroxides with detergent salts and/or organic surface-active agents are also described.

BACKGROUND OF THE INVENTION

This invention relates to a bleaching process and to bleaching compositions employing an organic bleaching agent.

The bleaching of fabrics and the like with hydrogen peroxide or with inorganic substances yielding hydrogen peroxide in solution is known to the art and such substances, in particular sodium perborate or percarbonate, have long been common ingredients of bleaching and detergent compositions. These bleaching agents are effective at temperatures near the boiling point of water, for example, over about 85° C.; however, these substances have little effect at temperatures from 35° C. to 65° C.

Certain organic peroxygen compounds have been disclosed as bleaching agents effective at these lower temperatures. One class includes the organic aliphatic and aromatic peroxycarboxylic acids, and especially the more effective aromatic percarboxylic acids such as those described in U.S. Pat. 3,075,921 issued Jan. 29, 1963 to Brocklehurst et al. These compounds, however, are generally unstable; they tend to lose their activity rapidly in storage, and in some cases may be explosive. Thus, they are difficult to handle in processing and in use. Furthermore, this instability is intensified by traces of metals such as iron, nickel, cobalt, copper and the like.

The organic peroxides, and in particular the diacyl peroxides, comprise another class of peroxygen bleaching agents. Some of these compounds are described in Belgian patent specification 603,768. These substances hydrolyze in the presence of water to form peroxycarboxylic acids, which are believed to be the substances actually responsible for the bleaching activity. The organic peroxides tend to be unstable and in some cases are explosive. Many are only slightly soluble in water, and therefore, hydrolyze slowly at moderate washing temperatures. Thus, little of the actual bleaching agent may be released in the duration of an ordinary washing process. Dibenzoyl peroxide is an example of an unstable and slightly-soluble peroxide compound.

Benzoyl succinyl peroxide is one of the preferred diacyl peroxides set forth in Belgian specification 603,768; this compound is soluble in water, under neutral or alkaline conditions. Nevertheless, it is unstable in detergent compositions. Explosivity tests indicate that it may detonate upon impact. Although detergent compositions are unlikely to be subjected in ordinary use to the impact applied in an impact test (as described in Example III hereafter),

a propensity to detonate under such conditions indicates that they may be dangerously unstable under other conditions.

SUMMARY OF THE INVENTION

It has now been found quite unexpectedly that the benzoyl glutaryl peroxides of this invention are stable in detergent compositions and are non-explosive, even in the presence of metal ions such as iron, nickel, cobalt, copper and the like. In spite of their improved stability, these benzoyl glutaryl peroxides, being soluble in alkaline washing and bleaching liquors, hydrolyze rapidly during a washing or bleaching process, forming an aromatic peroxy acid as the effective bleaching agent. The benzoyl glutaryl peroxides are, therefore, very valuable bleaching agents for use at temperatures below about 85° C.; they are also effective at higher temperatures.

In its process aspect, the present invention provides a process for bleaching textile materials which comprises treating such materials with an aqueous solution of a benzoyl glutaryl peroxide of the general formula

$$RCO{\cdot}OO{\cdot}CO(CH_2)_3CO_2H$$

where R is phenyl or substituted phenyl.

In its composition aspect, the present invention provides bleaching compositions containing a benzoyl glutaryl peroxide of the invention in combination with a detergent salt and/or organic surface active agent.

DETAILED DESCRIPTION OF THE INVENTION

The benzoyl glutaryl peroxides suitable herein are those corresponding to the hereinbefore described formula.

Preferred peroxides are those where the benzoyl radical is unsubstituted or is substituted by one or more chlorine, methyl or methoxy groups. Suitable substituted benzoyl glutaryl peroxides include m-chlorobenzoyl glutaryl peroxide, p-methylbenzoyl glutaryl peroxide, p-methoxybenzoyl glutaryl peroxide.

Ordinarily the peroxides of the invention are employed in a solution at a concentration which provides from 1 to 200 p.p.m. by weight of available oxygen in the solution. A preferred concentration is from 5 to 150 p.p.m., especially from 10 to 40 p.p.m.

The benzoyl glutaryl peroxides of the invention can be prepared in accordance with methods known in the art. Suitable methods of preparation include, for example, reaction of an aromatic peroxy acid with glutaric anhydride in a suitable solvent, or reaction of an aroylchloride with mono perglutaric acid in the presence of an equivalent weight of a base. The preparation of benzoyl glutaryl peroxide is disclosed by Zeit. f. Physiol. Chemie, 323, pp. 211–235 (1961), incorporated by reference herein.

In practice, it is usually convenient to incorporate the benzoyl glutaryl peroxides of the invention into a bleaching or bleaching and washing composition containing other desirable components. Such compositions are preferably, but not necessarily, particulate solids. The compositions can contain inorganic or organic detergent builder salts. They can contain, for example, alkaline inorganic builder salts such as the alkali metal carbonates, silicates, phosphates and polyphosphates. Suitable organic water-soluble builder salts include the aminopolycarboxylates, particularly sodium nitrilotriacetates, organic polyphosphonates such as ethane-1-hydroxy-1, 1-diphosphonates, sodium citrate, sodium gluconate and the like. The builder salts herein are employed in an amount of from 1% to 99% by weight of the compositions of the invention. Neutral diluent salts such as alkali metal chlorides or sulfates can be employed. Compatible water-soluble organic surface-active agents, including anionic, nonionic, zwitterionic and ampholytic detergents can also be present, for example, in an amount of up to 90% by weight. The amounts of these components, i.e., the in-

organic or organic builder salts and organic surface-active agents used, depend on both the nature of the organic detergent and the intended purpose of the products. Normally the proportions of such components will correspond to a weight ratio of builder to detergent of from about 30:1 to 1:4, preferably from 9:1 to 1:1.

Particularly suitable organic anionic detergents are the water-soluble soaps and the alkyl benzene sulfonates, especially linear alkyl benzene sulfonates, alkyl sulfates, olefin sulfates and other organic sulfates and sulfonates. Suitable nonionic detergents include the polyethylene oxide condensates with polypropylene oxides, e.g., the Pluronics (trade name), or with fatty alcohols, alkyl phenols, fatty acids and the like. Suitable detergents herein are those described in U.S. Pat. 3,351,558 to Roger E. Zimmerer at column 6, line 59 to column 9, line 69, incorporated herein by reference.

The compositions can also contain the usual minor components of conventional bleaching and washing compositions such as colors, perfume, tarnish inhibitors stabilizers for the bleach, optical brighteners, enzymes, dust preventatives, suds-enhancing or suds-depressing agents, abrasives and the like.

The compositions of the invention provide desirable oxidizing and bleaching functions to facilitate the removal of soils and stains on fabrics treated therewith. The compositions can be used in connection with conventional laundering operations such as soaking, washing, rinsing and the like to remove soils and stains from laundered fabrics, such as cottons, linens and the like.

Although the peroxides described hereinbefore are more stable during storage in detergent compositions than prior known water-soluble organic peroxy bleaching agents, it is desirable to provide protection from atmospheric or other moisture and from other components of the compositions. This can be effected for instance, by coating the peroxide with an inert material, or by mixing the peroxides with an inert or stabilizing substance and coating the mixture. Alternatively the mixture can be agglomerated or extruded in the form of "noodles," ribbons, flakes or the like. Other suitable methods of providing protection from moisture can be employed.

The proportion of the benzoyl glutaryl peroxide in the compositions of the invention should be such as to provide a concentration of available oxygen in the ranges defined hereinbefore when the compositions are used at the intended concentration in a bleaching or washing liquor. The compositions intended to be used at conventional concentrations for household washing would normally contain enough benzoyl glutaryl peroxide to provide from 0.1% to 3% by weight of the composition of available oxygen, preferably 0.2% especially from 0.2% to 1%.

The following examples illustrate the invention:

EXAMPLE I

Bleaching effect

Solutions were prepared containing 4 g. per liter of a detergent composition consisting of percent by weight:

Linear alkylbenzene sulfonate (alkyl chain C_{11} to C_{13})	17.6
Sodium toluene sulfonate	1.8
Sodium tripolyphosphate	46.2
Sodium silicate	7.3
Coconut monoethanolamide	1.8
Sodium carboxymethylcellulose	1.0
Sodium sulfate	12.4
Miscellaneous minor components	1.9
Moisture	10.0

together with

(a) sufficient sodium perborate to provide 100 p.p.m. available oxygen in the solution;

(b) sufficient benzoyl glutaryl peroxide to provide 10 p.p.m. available oxygen in the solution;

(c) sufficient benzoyl glutaryl peroxide to provide 100 p.p.m. available oxygen in the solution. Tea stained cotton cloth swatches were treated at 50° C. for 10 minutes in each solution then rinsed and dried. Comparison of the reflectance of the untreated and treated cloths indicated in case (a) 33% stain removal; (b) 38% stain removal; (c) 76% stain removal.

EXAMPLE II

Stability in detergent composition

The stabilities of a typical aromatic peroxy acid and of benzoyl succinyl peroxide and benzoyl glutaryl peroxide when mixed with detergent granules of composition given in Example I were compared. The percentage loss of active oxygen in 14 days storage at 21° C. in wax laminated cartons was:

	Percent
m-Chloro peroxybenzoic acid	85
Benzoyl succinyl peroxide	12
Benzoyl glutaryl peroxide	4
m-chloro-benzoyl glutaryl peroxide	5

EXAMPLE III

Explosivity

Samples were tested in an Impact Testing machine wherein 0.02 g. of substance was spread on a die of 1 square cm. area confined by a plunger of the same area. A 2 kg. weight was dropped on the plunger from 150 and 200 cms. In each case benzoyl succinyl peroxide detonated, benzoyl glutaryl peroxide did not detonate.

EXAMPLE IV

Bleaching performance in aqueous solution alone

Pieces of tea stained cotton cloth were washed for 10 minutes in solutions of the substances named below, each at a level to provide 100 parts per million available oxygen, at 50° C. The stain removal value measured as in Example I were:

	Percent
Benzoyl glutaryl peroxide	49.5
Sodium perborate	3
Dibenzoyl peroxide	Nil

EXAMPLE V

Stability in presence of sodium carbonate

Equal weights of sodium carbonate and the following peroxides were mixed and stored in wax-laminated cardboard cartons in a laboratory (at about 24° C.) for two weeks. The loss of available oxygen, by weight of that originally present was:

	Percent
(a) Benzoylglutaryl peroxide	3
(b) m-Chlorobenzoyl glutaryl peroxide	3
(c) Benzoyl succinyl peroxide	39
(d) Dibenzoyl peroxide	13

What is claimed is:

1. A process for bleaching textile materials which consists essentially of treating such materials with an aqueous solution of benzoyl glutaryl peroxide of the formula

$$RCO{\cdot}OO{\cdot}CO(CH_2)_3CO_2H$$

wherein R is phenyl or substituted phenyl; said substituted phenyl being substituted with one or more —Cl, —OCH_3 or —CH_3 radicals.

2. The process of claim **1** wherein R is phenyl.

3. The process of claim **1** wherein the peroxide is present at a concentration sufficient to provide from 1 to 200 parts per million by weight of available oxygen in solution.

4. The process of claim **1** wherein the peroxide is present at a concentration sufficient to provide from 10 to 40

parts per million by weight of available oxygen in solution.

5. The process of claim 1 wherein there is present in the aqueous solution a mixture of water-soluble organic detergent and water-soluble builder salt in a ratio of builder salt to detergent of from 30:1 to 1:4.

6. A bleaching composition consisting essentailly of a mixture of a water-soluble organic detergent selected from the group consisting of anionic, nonionic, Zwitterionic and ampholytic detergents and a water-soluble inorganic or oragnic detergency builder salt in a ratio of detergency builder salt to detergent of from 30:1 to 1:4; and a benzoyl peroxide bleaching agent of the formula

$$RCO{\cdot}OO{\cdot}CO(CH_2)_3CO_2H$$

wherein R is phenyl or substituted phenyl; said substituted phenyl being substituted with one or more —Cl, —OCH_3 or —CH_3 radicals.

7. The bleaching composition of claim 6 wherein R is phenyl.

8. The bleaching composition of claim 7 having sufficient benzoyl glutaryl peroxide to provide from 0.1% to 3% by weight of the composition of available oxygen.

9. The composition of claim 8 wherein the ratio of builder salt to detergent is from about 3:1 to 100:1, especially from 9:1 to 1:1.

References Cited

UNITED STATES PATENTS

1,767,543	6/1930	McKee	8—111
3,026,166	3/1962	Gallagher et al.	8—111

MAYER WEINBLATT, Primary Examiner

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252—95, 99, 186