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3,756,775

BLEACHING PROCESS AND COMPOSITION
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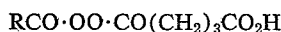
Int. Cl. D06f 3/02

U.S. Cl. 8—111

9 Claims

ABSTRACT OF THE DISCLOSURE

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



wherein R is phenyl or substituted phenyl and an inorganic perhydrate is disclosed. Bleaching compositions containing such peroxides and perhydrates 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 and an inorganic perhydrate.

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 peroxydicarboxylic 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 peroxydicarboxylic 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 condi-

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tions 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 peroxide bleaching agents of this invention are stable in detergent compositions and have a reduced tendency to cause color or fabric damage when employed in combination with an inorganic perhydrate. In addition, they are nonexplosive, 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°; 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



where R is phenyl or substituted phenyl and an inorganic perhydrate.

In its composition aspect, the present invention provides bleaching compositions containing a benzoyl glutaryl peroxide and an inorganic perhydrate 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.

A primary function of an oxidizing bleaching agent is to react chemically with and to oxidize stains, thereby reducing their color and/or making them more susceptible to washing action. On the other hand, such agents should not decolorize or alter appreciably dyestuffs (which might be considered as intentional "stains"), or cause damage to fabrics themselves, but no effective bleaching agent is perfect in these respects. It has now been found that the tendency of benzoyl glutaryl peroxides to cause color or fabric damage, and its tendency to cause yellowing of nylon fabrics, is reduced if an inorganic perhydrate, is present with it in the bleaching liquor.

By inorganic perhydrates are meant compounds providing hydrogen peroxide in aqueous solution, such as sodium perborate, percarbonate, perphosphate, or hydrogen

peroxide itself. Potassium and other suitable salts can also be used. This mixture provides slightly less bleaching action than the benzoyl glutaryl peroxide alone but considerably more, at temperature below about 85° C., than perhydrate alone, and provides a better combination of bleaching effect and lack of color or fabric damage than is provided by either component alone.

Preferred perhydrates are those named above, especially sodium perborate. Hydrogen peroxide as such may be used in bleaching liquors and in the process of the invention. Its use in concentrated compositions, though within the scope of the invention, would often lead to difficulty in obtaining stable products. The amount of perhydrate is preferably such that the weight ratio of available oxygen in the benzoyl glutaryl peroxide to that in the perhydrate is from 3:1 to 1:5, especially in the range 1:1 to 1:5.

In practice, it is usually convenient to incorporate the benzoyl glutaryl peroxide and inorganic perhydrate 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 inorganic 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.

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 washig 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

- sufficient sodium perborate to provide 100 p.p.m. available oxygen in the solution;
- sufficient benzoyl glutaryl peroxide to provide 10 p.p.m. available oxygen in the solution;
- 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 values measured as in Example I were:

	Percent
Benzoyl glutaryl peroxide	49.5
Sodium perborate	3
Dibenzoyl peroxide	Nil

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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) Benzoyl glutaryl peroxide -----	3
(b) m-Chlorobenzoyl glutaryl peroxide -----	3
(c) Benzoyl sucinyl peroxide -----	39
(d) Dibenzoyl peroxide -----	13

EXAMPLE VI

A typical heavy duty detergent in combination with a bleaching agent was prepared having the following formula:

Sodium linear alkylbenzene sulfonate -----	9
Sodium tallow alkyl sulfate -----	5
Sodium toluene sulfonate -----	1
Soap (tallow/coconut oil) -----	4
Sodium tripolyphosphate -----	45
Sodium silicate -----	10
Coconut ethanolamides -----	2
Sodium carboxymethylcellulose -----	1
Sodium sulfate -----	11
Moisture -----	10
Miscellaneous (impurities, perfume, etc.) -----	2
	100

Washing and bleaching solutions were made up in tap water (about 175 p.p.m. hardness as CaCO₃) containing per liter:

- (i) 4.75 g. Composition A 0.25 g. BGP
 - (ii) 4.55 g. Composition A 0.25 g. BGP 0.2 g. PB4
 - (iii) 4.45 g. Composition A 0.25 g. BGP 0.3 g. PB4
 - (iv) 4.25 g. Composition A 0.25 g. BGP 0.5 g. PB4
 - (v) 4.15 g. Composition A 0.25 g. BGP 0.6 g. PB4
- BGP means Benzoyl glutaryl peroxide
PB4 means sodium perborate tetrahydrate

Stain removal

Tea stained cotton swatches were washed in these solutions in a miniature washing machine at 50° C. for 10 minutes. They were removed, rinsed in cold tap water, dried and their reflectance measured and compared with that before washing, percent stain removal being measured as:

$$100 \times \frac{\text{Reflectance after bleach} - \text{Reflectance before bleach}}{100 - \text{Reflectance before bleach}}$$

Values obtained were:

Solution:	Percent stain removal
(i) -----	71
(ii) -----	65
(iii) -----	64
(iv) -----	68
(v) -----	68

Fabric damage

Test pieces of nylon, cotton, and terylene-cotton mixture were washed 10 times in solutions (i), (iii) and (v) at 50° C. After each wash they were rinsed in cold tap water and dried. Fabric damage was denoted by loss of tensile strength and the figures given below represent the average percentage loss of tensile strength of all the fabrics.

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Solution:	Percent loss of tensile strength
(i) -----	13
(iii) -----	9
(v) -----	10

Nylon yellowing

Test pieces of nylon, treated with optical brightener during manufacture were placed in solutions (i), (ii), (iii) and (iv) at 50° C., soaked overnight and allowed to cool naturally to room temperature. Fresh solutions were heated to 50° C. and the fabrics were washed at this temperature for 10 minutes, rinsed in cold tap water and dried. This cycle was repeated 10 times. The whiteness or yellowness of the fabrics before and after treatment was measured by means of a Hunter Color Difference Meter (manufactured by Hunter Associates Laboratory's Inc.) on a scale where increasing negative values indicate increased yellowness.

Values obtained were:

Solution:	
(i) -----	-38
(ii) -----	-23
(iii) -----	-11
(iv) -----	-8

EXAMPLE VII

Washing and bleaching solutions were made as in Example VI but containing per liter

- (vi) 4.25 g. Composition A 0.25 g. BGP 0.5 g. PB4
- (vii) 4.8 g. Composition A 0.20 g. BGP

Stain removal tests and nylon yellowing tests were conducted as in Example VI. The results were:

Stain removal

Solution:	Percent
(vi) -----	68
(vii) -----	67

Nylon yellowing

Solution:	
(vi) -----	-4
(vii) -----	-22

A level of BGP which gives the same or slightly less stain removal than mixed BGP/perborate produces yellowing of nylon.

What is claimed is:

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



wherein R is phenyl or phenyl substituted with one or more —Cl, —OCH₃ or —CH₃ radicals; and an inorganic perhydrate capable of providing hydrogen peroxide in said solution and providing a weight ratio of available oxygen from the benzoyl glutaryl peroxide to that of the inorganic perhydrate of from 3:1 to 1:6.

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

3. The process of claim 1 wherein the benzoyl glutaryl 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 benzoyl glutaryl peroxide is present at a concentration sufficient to provide from 10 to 40 parts per million by weight of available oxygen in solution.

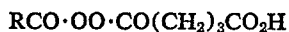
5. The process of claim 1 wherein the inorganic perhydrate is selected from the group consisting of sodium perborate, sodium perphosphate and sodium percarbonate.

6. The process of claim 4 wherein the weight ratio of available oxygen of said benzoyl glutaryl peroxide to that of said perhydrate is from 1:1 to 1:6.

7. A bleaching composition consisting essentially of a mixture of a water-soluble organic detergent selected from

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the group consisting of anionic, nonionic, zwitterionic and ampholytic detergents and water-soluble inorganic or organic detergency builder salt in a ratio of builder salt to detergent of from 30:1 to 1:4, a benzoyl glutaryl peroxide bleaching agent of the formula



wherein R is phenyl or substituted with one or more —Cl, —OCH₃ or —CH₃ radicals; and an inorganic perhydrate 10 capable of providing hydrogen peroxide in aqueous solution and providing a weight ratio of available oxygen from the benzoyl glutaryl peroxide to that of the inorganic perhydrate of from 3:1 to 1:6.

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

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

References Cited

UNITED STATES PATENTS

3,026,166 3/1962 Gallagher ----- 8-111

MAYER WEINBLATT, Primary Examiner

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252-95, 99, 186

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,756,775 Dated September 4, 1973

Inventor(s) Kjell Torsten Nordfalt

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 3, line 4 "temperature" should read --temperatures--

Column 3, line 16 "1:5" and "1:5" should read --1:6-- and --1:4-- respectively

Column 3, line 20 "compoents" should read --components--

Column 5, line 12 "suciny1" should read --succiny1--

Column 7, line 9 "substituted" should read --phenyl substituted--

Signed and sealed this 10th day of September 1974.

(SEAL)
Attest:

McCOY M. GIBSON, JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents

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