

United States Patent [19]

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[11] 3,773,673

[45] Nov. 20, 1973

[54] BLEACHING COMPOSITION

3,075,921 1/1963 Brocklehurst et al. 252/99

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[22] Filed: Nov. 20, 1972

[21] Appl. No.: 308,075

Related U.S. Application Data

[63] Continuation of Ser. No. 96,650, Dec. 9, 1970,
abandoned.

[52] U.S. Cl. 252/95, 252/99, 8/111

[51] Int. Cl. C11d 7/54

[58] Field of Search 252/95, 99; 8/111

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[57] ABSTRACT

Bleaching compositions having mixtures of persulfate bleaching compounds and organic peroxy-compounds in proportions such that the weight ratio of available oxygen from the persulfate to that from the organic peroxy compounds is up to 3:1. The compositions are particularly useful for washing and bleaching at lower temperatures. The bleaching compositions can be employed with detergent compounds to provide bleaching and detergent compositions having from 0.1 to 3 percent available oxygen by weight. A method aspect of the invention comprises treating fibrous materials in aqueous solution with the mixture of bleaching agents of the invention at a concentration of from 1 to 100 parts per million by weight of available oxygen.

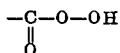
14 Claims, No Drawings

BLEACHING COMPOSITION

This application is a continuation of U.S. Application 96,650, filed December 9, 1970 now abandoned.

The invention relates to a bleaching composition comprising a synergistic mixture of oxygen bleaching agents. More particularly, this invention is based on the surprising discovery that a particular mixture of oxygen bleaching agents is more effective at a given level of available oxygen than either of its components alone.

Among the most commonly used inorganic oxygen bleaching agents are sodium perborate, percarbonate and the like. These compounds have little bleaching activity at temperatures below about 85°C. Other known types of inorganic bleaching agents, which are more effective at temperatures below 85°C, include persulfuric acid (sometimes known as Caro's Acid) and its salts and acid salts, and mixed salts, such as Oxone (trade name) which consists essentially of the compound KHSO_4 , K_2SO_4 , 2KHSO_5 . Among organic peroxy-compounds known to have bleaching properties are the aliphatic and aromatic percarboxylic acids based on the radical



It has now surprisingly been found that certain mixtures of persulfates and organic peroxy-compounds have more bleaching effect than members of either class alone when used at the same concentration of available oxygen.

The "available oxygen" is that which is free to react with oxidizable substances, for instance one atom for each molar equivalent of an —SO_3 or $\text{—CO}_3\text{H}$ radical. The amount is usually expressed as a proportion by weight of a relevant compound, mixture or composition.

According to the invention there is provided a bleaching composition which comprises a mixture of a persulfate and an organic peroxy-compound in proportions such that the weight ratio of available oxygen derived from the persulfate to that derived from the organic peroxy-compound is up to 3:1.

The invention also provides detergent compositions containing such a mixture of bleaching agents and a detergent substance.

The invention also provides a method of bleaching fibrous materials by treating them in an aqueous solution containing from 1 to 100 parts per million by weight of available oxygen derived from such a mixture of bleaching agents.

Preferred inorganic persulfates are alkali metal or ammonium persulfates, such as sodium or potassium monopersulfate, and particularly the mixed salt KHSO_4 , K_2SO_4 , 2KHSO_5 , or the corresponding sodium salt.

Organic peroxy-compounds are preferably the aliphatic or aromatic percarboxylic acids and their alkali metal and ammonium salts. Among the aliphatic peracids may be named peracetic acid, perpropionic acid, up to perlauroic acid and the like. The preferred peracids are aromatic peracids such as perbenzoic acid and nuclear-substituted perbenzoic acids, especially those having a melting point above 50°C, such as those described in British Patent Specification 886,188. Especially preferred is p-methoxyperbenzoic acid.

The mixed bleaching agent should preferably be present in the bleaching solution at a concentration such as to provide from 1 to 100 parts per million (ppm) by weight of available oxygen in the solution. Below about 1 ppm little bleaching effect is observed; above about 70 ppm there may be no advantage for the mixture over the peracid alone. A preferred range of available oxygen content is from 10 to 70 ppm.

Addition of quite small proportions of persalt to the organic peroxy-compounds provides mixtures performing better (at constant available oxygen level) than the peroxy-compound alone, but it is preferred to employ mixtures wherein the weight ratio of available oxygen derived from the persulfate to that derived from the peroxy compound is at least 1:10. At the other extreme there is little or no advantage for the mixture over the peracid alone when the ratio is greater than 3:1, and preferably it is not greater than 1:1. The optimum ratio, defined as that which provides the maximum bleaching effectiveness per unit of available oxygen, is generally approximately 1:2. As will be understood, the economic optimum ratio may be somewhat different depending upon the relative cost of the two bleaching components.

The bleaching mixtures are preferably used at pH (of the bleaching liquor) in the range from 8.5 to 11.5, especially from 9.5 to 10.5. They are effective at moderate washing temperatures, below about 85°C, and are particularly valuable for washing and bleaching at temperatures not exceeding 60°C, for instance within the range from 40° to 55°C. Though they are effective at temperatures of about 85°C up to the boil, other and well-known bleaching agents, such as the perhydrates, are also effective at these temperatures, so that the compositions of the invention find their greatest utility when used for washing and bleaching at lower temperatures.

The bleaching agents of the invention can be used in the presence of compatible water-soluble organic detergents to provide a detergent composition, which can contain other ingredients such as inorganic builder salts and/or organic sequestrant builder salts. Particularly suitable organic detergents are the anionic detergents such as soap, alkylaryl sulfonates, alkyl sulfates, alkane sulfonates, olefin sulfonates, fatty acid isethionates and fatty acyl taurides. Nonionic zwitterionic and cationic detergents which are substantially unaffected in solution by the bleaching agents can also be used. Suitable inorganic salts and builder salts include those commonly used in detergent compositions such as alkali metal ortho-, pyro- and tripolyphosphates, and more condensed phosphates, and alkali metal carbonates, bicarbonates, silicates, sulfates and borates. Organic alkaline builder salts such as nitrilotriacetates, ethylenediamine tetraacetates, ethane-1,1-hydroxy-1,1-diphosphonates and the like can also be used. The sodium or potassium, especially the sodium salts, are most commonly employed. The bleaching agents can either be used in solution together with a suitable combination of these substances or they can constitute part of a detergent composition containing at least some of these components. Preferably such detergent compositions are particulate, either flowable powders or aggregates or briquettes.

In cases where the moisture or some other components of the detergent composition might interact undesirably with the solid bleaching agents, it is desirable

to take precautions to minimize contact between the bleaching agents and between them and other components of the detergent composition. This can be achieved by pelletizing or granulating the bleaching agents individually, together, or in admixture with an inert substance or one which has a stabilizing effect, such as certain inorganic salts. This considerably reduces the area of contact between the bleaching agents and the other components. Alternatively, the bleaching agents, individually or together, or in admixture with inert or stabilizing substances, can be coated with an inert protective material which is removed by solution, melting or abrasion in the washing process.

The detergent compositions or the aqueous bleaching solutions, can contain other compatible minor ingredients commonly employed in such compositions, such as soil-suspending agents, for example carboxymethyl cellulose; copolymers of methyl vinyl ether and maleic anhydride and other water-soluble polymeric substances; suds-controlling agents, such as fatty acid ethanolamides to improve suds stability; or nonionic detergents, high molecular weight (C_{16} and over) saturated fatty acids or their soaps, and the like to depress sudsing; optical brighteners; tarnish inhibitors; proteolytic, amylolytic or lipolytic enzymes; dyes; perfume; and the like.

It is of course preferred to incorporate the bleaching agents in detergent compositions in proportions such that when the detergent composition is used at the usual and proper concentration for satisfactory washing performance, the concentration of available oxygen in the washing solution is in the ranges described hereinbefore. Thus, in conventional type heavy duty household detergents an available oxygen content in the range about 0.1 to 3 percent by weight of the composition is often suitable, especially about 0.25 to 1 percent.

The invention is illustrated by the following Examples.

EXAMPLE I

A solution was prepared containing 4 g. per liter of a detergent composition consisting of, by weight;
Linear alkyl benzene sulfonate (alkyl chain C_{11-13}) — 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%

The solution was warmed to 49°C. A mixture of potassium monopersulfate in the form of "Oxone" (trade name) and of p-methoxyperbenzoic acid in proportions such as to provide 22.2 parts per million available oxygen from "Oxone" and 44.5 parts per million from p-methoxy perbenzoic acid were added to the solution, and the pH adjusted to 10.0 by addition of dilute alkali. Tea-stained cloth swatches were treated at 49°C for 10 minutes in this solution, rinsed and dried. Comparison of the reflectance of the untreated and treated cloths indicated 77.1 percent stain-removal.

Comparative tests using "Oxone" alone, and p-methoxyperbenzoic acid alone, each at a concentration such as to provide 66.7 parts per million of available

oxygen in the solution gave 53.5 and 72.5 percent stain-removal, respectively.

EXAMPLE II

In a test similar to that of Example I using the same bleaching agents in proportions such that "Oxone" provided 5 parts per million available oxygen and p-methoxy perbenzoic acid provided 15 parts per million, stain-removal values were,

Mixture — 58.5%

P-methoxy perbenzoic acid alone at 20 ppm available oxygen — 52.3%

"Oxone" alone at 20 ppm available oxygen — 38.3%

EXAMPLE III

A bleaching test was carried out in similar conditions to those of Example I, but reating the stained test cloths in a solution only containing "Oxone" and perbenzoic acid (adjusted to pH 9.5) at levels such that each provided 17.5 parts per million of available oxygen. The results were compared with those given by each agent alone at a concentration providing 35 ppm available oxygen. Stain removal figures were:

Mixture — 53%

Perbenzoic acid — 45%

"Oxone" — 28%

What is claimed is:

1. A bleaching composition which consists essentially of a mixture of an alkali metal or ammonium monopersulfate and an organic peroxy-compound, in proportions such that the weight ratio of available oxygen derived from the monopersulfate to that derived from the peroxy compound is from 1:1 to 1:3; said organic peroxy-compound being selected from the group consisting of perbenzoic acid, p-methoxy perbenzoic acid and the alkali metal and ammonium salts thereof.

2. The bleaching composition of claim 1 wherein the monopersulfate is an alkali metal monopersulfate.

3. The bleaching composition of claim 1 wherein the monopersulfate consists essentially of a mixed salt of formula $MHSO_4$, M_2SO_4 , and $2MHSO_5$ wherein M is potassium or sodium.

4. The bleaching composition of claim 1 wherein the organic peroxy compound is perbenzoic acid or an alkali metal or ammonium salt thereof.

5. The bleaching composition of claim 1 wherein the organic peroxy compound is p-methoxy perbenzoic acid.

6. A bleaching and detergent composition consisting essentially of a water-soluble organic detergent; and the mixture of monopersulfate and organic peroxy-compound bleaching compounds of claim 1; the weight ratio of available oxygen derived from the monopersulfate to that derived from the peroxy compound being up to 3:1; the bleaching and detergent composition having from 0.1 to 3 percent available oxygen by weight.

7. The bleaching and detergent composition of claim 6 wherein there is also present an inorganic builder salt or organic sequestrant builder salt or mixtures thereof.

8. The bleaching and detergent composition of claim 7 wherein the available oxygen by weight of the composition ranges from 0.1 to 3 percent.

9. The bleaching and detergent composition of claim 8 wherein the available oxygen by weight of the composition ranges from 0.25 to 1 percent.

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10. A method of bleaching fibrous materials which comprises treating them in an aqueous solution of the composition of claim 1, the concentration of said composition being such that there is present in the aqueous solution from 10 to 70 parts per million by weight of available oxygen.

11. The method of claim 10 wherein the bleaching solution has a pH of from 8.5 to 11.5.

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12. The method of claim 11 wherein the pH value is from 9.5 to 10.5.

13. The method of claim 10 wherein the solution is at a temperature not exceeding 60°C.

14. The method of claim 13 wherein the solution is at a temperature within the range from 40°C to 55°C.

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