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L. H. DIAMOND ET AL

QUATERNARY AMMONIUM PEROXYSULFATES

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INVENTORS
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BY
A class of bleaching agents has been found which is effective in giving a high degree of brightness without degrading the fabric during bleaching. These compounds are quaternary ammonium peroxy sulfates having the formula:

\[
\text{R}_1 \text{N-R}_2 \text{R}_3 \text{R}_4 \text{HBO}_4
\]

and diquaternary ammonium peroxydissulfates having the formula:

\[
\text{R}_1 \text{N-R}_2 \text{R}_3 \text{R}_4 \text{S}_2 \text{O}_4
\]

in which \( \text{R}_1, \text{R}_2, \text{R}_3 \) and \( \text{R}_4 \) may be saturated aliphatic, saturated cycloaliphatic or aromatic groups having up to 18 carbon atoms which are not oxidized by peroxy sulfates and which are attached to the nitrogen atoms through a carbon atom.

In addition, certain of these compounds have also been found useful as fabric softeners, namely those quaternary ammonium compounds in which at least one of the alky groups has from about 12 to about 18 carbon atoms.

This is a division of application Ser. No. 365,874, filed May 8, 1964, now U.S. Patent 3,563,902 issued on Nov. 21, 1967.

The present invention relates to an improved class of bleaching agents, and more particularly to quaternary ammonium peroxy sulfates and diquaternary ammonium peroxydissulfates (hereinafter termed peroxy sulfates).

In the process of laundering textile garments in domestic washing machines, it is common to employ a bleaching agent in addition to a detergent to maintain the original whiteness of the garments after laundering. The bleaching agents which are commonly in use include such compounds as sodium hypochlorite, chlorinated isocyanuric acids, and potassium persulfate.

These bleaching agents have been found to have certain drawbacks. For example, sodium hypochlorite and chlorinated isocyanuric acids tend to cause a measurable amount of fabric degradation during bleaching and are capable of causing localized overbleaching by direct contact of the bleach with the fabric. Bleaching with potassium monopersulfate reduces fabric degradation, but the bleaching action is inferior to sodium hypochlorite. Further, potassium monopersulfate does not have a good shelf life and thus loses its bleaching effectiveness on extended storage.

As a result, there is a need for an effective bleaching agent that is more active than the milder bleaching agents in common use but which does not cause any measurable degradation of the fabric during the bleaching operation.

It is an object of the present invention to provide an active, stable bleaching agent which is effective in giving a high degree of brightness without degrading the fabric during bleaching.

We have now found that quaternary ammonium peroxy sulfates having the formula

\[
\text{R}_1 \text{N-R}_2 \text{R}_3 \text{R}_4 \text{HBO}_4
\]

are effective bleaching agents for bleaching fabrics and have good storage stability. In the above formulations, \( \text{R}_1, \text{R}_2, \text{R}_3 \) and \( \text{R}_4 \) may be saturated aliphatic, saturated cycloaliphatic or aromatic groups having up to 18 carbon atoms which are not oxidized by peroxy sulfates and which are attached to the nitrogen atom through a carbon atom. The aliphatic groups may be straight chained, branch chained, or attached to form a heterocyclic group.

We have found that certain of these quaternary ammonium compounds are effective as fabric softeners as well as bleaching agents and can be employed for softening textiles while bleaching. The quaternary ammonium compounds useful for this purpose are those having only saturated alkyl chains on the quaternary ammonium residue and in which at least one of the alkyl groups has from about 12 to about 18 carbon atoms in the chain.

In accordance with the present invention, the quaternary ammonium peroxy sulfates and the diquaternary ammonium peroxydissulfates are produced by reaction of a quaternary ammonium salt (preferably one in which the anion of the salt is a halogen element) and an inorganic mono- or diper sulfate. Typical reactions proceed according to the following equations:

\[
\text{I} \quad \text{R}_1 \text{N-R}_2 \text{Cl} + \text{KHSO}_4 \rightarrow \text{R}_1 \text{N} + \text{R}_2 \text{HBO}_4 + \text{KCl}
\]

\[
\text{II} \quad \text{R}_1 \text{N-R}_2 \text{Cl} + \text{K}_2 \text{S}_2 \text{O}_7 \rightarrow \text{R}_1 \text{N} + 2\text{R}_2 \text{HBO}_4 + 2\text{KCl}
\]

where \( \text{R}_1, \text{R}_2, \text{R}_3 \), and \( \text{R}_4 \) are saturated aliphatic, saturated cycloaliphatic, or aromatic groups having up to about 18 carbon atoms which are not oxidized by peroxy sulfates and which are attached to the nitrogen atom through a carbon atom. An alternate method for preparing monopersulfates is carried out by reacting quaternary ammonium hydroxides with Caro's acid solutions.

The particular quaternary ammonium salt precursor which is chosen will depend upon the requirements of the final quaternary ammonium persulfate. For example, if the final product is to be used for both softening and bleaching of textiles or in detergent applications, a quaternary ammonium salt having all alkyl groups, at least one of which is a fatty alkyl group, is preferred. Examples of these are dodecyl trimethyl ammonium chloride, di-hydrogenated tallow dimethyl quaternary ammonium chloride, and others. If the final product is to be used only for bleaching, lower molecular weight quaternary ammonium salt precursors can also be used with good effect such as tetramethyl ammonium chloride or tetraethyl ammonium chloride.

Most inorganic persulfate reagents can be used in making up the quaternary ammonium persulfates, but for economic reasons, the commercially available per sul-
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fates, e.g. the ammonium, potassium and sodium mono-
peroxysulfates and dipersulfates, are preferred. For example,
in the preparation of quaternary ammonium monoper-
oxysulfates, potassium monopersulfate (potassium carbo-
rate) has been found most suitable.

In the preparation of the quaternary ammonium per-
oxymonosulfates, low reaction temperatures should be
employed, preferably not above 20°C. Low tempera-
tures are required because these compounds have such a
high activity that they will react at higher tempera-
tures with the salt which is produced in situ to liberate
free chlorine, and to convert the persulfate compound
to a sulfate. Preferred reaction temperatures are from
about zero to about 20°C.

In the production of diquaternary ammonium per-
oxymonosulfates, reaction temperatures of zero to 20°C
are preferred but either higher or lower reaction tem-
peratures can be employed since the diquaternary am-
monium peroxysulfates do not react with any of the
salts formed in situ. Lower temperatures are preferred
but only to prevent the final product from being soluble
in the reaction medium. At low temperatures, i.e. 0 to
20°C, the final product will crystallize from the re-
action medium with a minimum of the product remain-
ing soluble in the mother liquor. The use of temperatures
substantially below 0°C should also be avoided because,
at these lower temperatures, some of the starting ma-
terial may crystallize out of solution without being re-
aacted and therefore will contaminate the final product.

The reaction media employed depends, to a large extent,
upon the solubility of the final product in the reaction
media. It is chosen so that the final product is relatively insoluble in the reaction media while the precursor feed
reactants remain soluble therein. For example, in the
preparation of higher molecular weight, quaternary
ammonium peroxymonosulfates and diquaternary ammon-
ium peroxysulfates, water is preferred because the final
product is relatively insoluble in an aqueous reaction media whereas the feed reactants and the by-product salt are
sufficiently soluble to dissolve therein. In the case of lower
molecular weight quaternary ammonium peroxymonosulfates and diquaternary ammon-
ium peroxysulfates, a selective organic solvent media is preferred because the final product has a high
solubility in water and recovery of the final product from
a water medium would be extremely difficult. Suitable
organic reaction media include aqueous methanol, di-
methyl formamide, mixtures thereof, and isopropyl alco-
hol-aqueous mixtures.

The peroxysulfates which are suitable as bleaching
agents and the present invention are those which have
groups attached to the nitrogen atom that are not oxidiza-
able by any peroxysulfate, including both monoperox-
sulfates and dipersulfates. These groups, which are
attached to the nitrogen atom through a carbon atom,
may be saturated aliphatic, saturated cycloaliphatic, or
aromatic groups. The aliphatic and cycloaliphatic groups
must be saturated in order to be non-reactive with a per-
oxysulfate. The aliphatic and cycloaliphatic groups may be
unsubstituted or may contain substituents that are non-
oxidizable by peroxysulfates. Examples of aliphatic or
cycloaliphatic substituents that are non-oxidizable include
carboxyl, alkoxyl, ester, amido and nitro groups. The
aliphatic groups may also have phenyl substituents which
are non-oxidizable and which conform to the require-
ments of aromatic groups set forth below. Substituents
which can be oxidized on an aliphatic or cycloaliphatic
group of which therefore are unacceptable include amino,
hydroxyl, cyano, keto, halogens (except fluorine)
and aldehydes.

In the case of aromatic groups, e.g. phenyl groups,
attracted to the nitrogen atom, these may be unsub-
stituted or contain substituents such as carboxyl, alkoxyl,
ester, amide, nitro and halogen groups. The aromatic
groups may also have aliphatic substituents which are
chloride dissolved in 75 grams of methanol was poured into a 250 ml. beaker. To the solution was added, with stirring, 6.85 g. of ammonium persulfate dissolved in 25 g. of dimethyl formamide. The reaction mixture was cooled to approximately 2 to 3° C. with an ice-water bath. An insoluble product crystallized from the reaction mixture and was separated from the mother liquor by filtration. The crude product was washed three times with 25 ml. each of cold methanol and was dried in a Rinco evaporator under reduced pressure. A white crystal material was obtained weighing 9.5 g. It had an active oxygen content of 4.73% by weight as determined by iodometric titration. The crude product was purified by recrystallization from methanol and analyzed:

<table>
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<tr>
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<th>Percent</th>
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<tr>
<td>Theory</td>
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<tr>
<td>Carbon</td>
<td>28.22</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>7.11</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>3.25</td>
</tr>
<tr>
<td>Sulfur</td>
<td>18.84</td>
</tr>
<tr>
<td>Active Oxygen</td>
<td>7.70</td>
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<tr>
<td>Chloride</td>
<td>None</td>
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The product was identified as tetramethyl ammonium diperoxysulfate.

**EXAMPLE 2**

The same procedure used in Example 1 was repeated except that 14.5 grams of tetraethyl ammonium bromide was used instead of the tetramethyl ammonium chloride. A white, crystalline product weighing 11 grams was recovered from the Rinco evaporator. It had an active oxygen content of 3.49% by weight. The crude product was purified by recrystallization from methanol and analyzed:

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>Theory</td>
<td>Found</td>
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<tr>
<td>Carbon</td>
<td>43.45</td>
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<tr>
<td>Hydrogen</td>
<td>8.01</td>
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<tr>
<td>Nitrogen</td>
<td>6.10</td>
</tr>
<tr>
<td>Sulfur</td>
<td>14.17</td>
</tr>
<tr>
<td>Active Oxygen</td>
<td>1.68</td>
</tr>
<tr>
<td>Bromide</td>
<td>None</td>
</tr>
</tbody>
</table>

The product was identified as dodecyl-trimethyl ammonium diperoxysulfate.

**EXAMPLE 3**

An 11.5 g. sample of Arquad 12 was poured into a 250 ml. beaker and mixed with 2.16 g. of ammonium persulfate dissolved in about 10 ml. of water. Arquad 12 is a 50% solution of dodecyl-trimethyl ammonium chloride in aqueous isopropyl alcohol. No solid formation was observed in the reaction mixture at ambient temperature. The mixture was then slowly added to a liter of cold water with vigorous agitation and white solids commenced to precipitate from the solution. The reaction mixture was then cooled to about 0° C. and the crystallized product was filtered from the mother liquor, washed twice with cold water, and dried on a Rinco evaporator under reduced pressure. The product was a white solid weighing 5 grams and having an active oxygen content of 2.49% by weight. The product was purified by recrystallization from methylene chloride and analyzed:

<table>
<thead>
<tr>
<th></th>
<th>Percent</th>
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</thead>
<tbody>
<tr>
<td>Theory</td>
<td>Found</td>
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<tr>
<td>Carbon</td>
<td>65.52</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>10.59</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>4.32</td>
</tr>
<tr>
<td>Sulfur</td>
<td>9.88</td>
</tr>
<tr>
<td>Active Oxygen</td>
<td>2.47</td>
</tr>
</tbody>
</table>

**EXAMPLE 4**

The same procedure used in Example 3 was repeated except that the reagents employed were 11.5 g. of Arquad 16 in place of Arquad 12 and 1.78 g. of ammonium persulfate. Arquad 16 is a 50% solution of palmitoyltrimethyl ammonium chloride. The resultant product was a white solid weighing 5.6 g. and having an active oxygen content of 2.07% by weight. The product was recrystallized from methylene chloride and analyzed:

<table>
<thead>
<tr>
<th></th>
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</thead>
<tbody>
<tr>
<td>Theory</td>
<td>Found</td>
</tr>
<tr>
<td>Carbon</td>
<td>59.96</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>11.15</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>3.98</td>
</tr>
<tr>
<td>Sulfur</td>
<td>2.19</td>
</tr>
<tr>
<td>Active Oxygen</td>
<td>2.10</td>
</tr>
</tbody>
</table>

The product was identified as palmitoyl-trimethyl ammonium diperoxysulfate.

**EXAMPLE 5**

The procedure of Example 3 was repeated except that the reagents employed were 5.75 g. of bisobutylphenoxyethyl dimethyl benzylammonium chloride (Hyamine 1622) and 1.21 g. of ammonium persulfate. A white solid product weighing 5.0 g. and having an active oxygen content of 1.73% by weight was obtained. It was identified as bisobutylphenoxyethyl dimethyl benzylammonium diperoxysulfate.

**EXAMPLE 6**

The procedure of Example 3 was repeated except that the reagents employed were 4.4 g. of Arquad 2HT was dissolved in 150 ml. of methanol and poured into a 400 ml. beaker. Arquad 2HT is a proprietary composition containing 55% by weight of dimethyl di-hydrogen tallow ammonium chloride. The fatty alkyl groups in this proprietary composition contain approximately 65% of 16, 30% of 18, and 5% of C12 alkyl chains. The Arquad 2HT solution was cooled to 5° C. A solution made up of 15 g. of potassium monopersulfate (potassium carinate) assaying 88% dissolved in 150 ml. of distilled water was then added to the Arquad 2HT solution. The reaction mixture was stirred and further cooled to 0° C. A white solid product crystallized from the reaction mixture and was separated by filtration from the mother liquor. The resulting solids were washed twice with 100 ml. of a cold (-5° C.) methanol-water mixture and dried in a Rinco evaporator under reduced pressure. The resultant white solid product weighed 36 g. and had an active oxygen content of 2.20% by weight. A sample of the product was purified by recrystallization from methanol and analyzed:

<table>
<thead>
<tr>
<th></th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theory</td>
<td>Found</td>
</tr>
<tr>
<td>Carbon</td>
<td>67.45</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>2.15</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>11.98</td>
</tr>
<tr>
<td>Sulfur</td>
<td>4.90</td>
</tr>
<tr>
<td>Active Oxygen</td>
<td>2.47</td>
</tr>
</tbody>
</table>
The resultant product was identified as dimethyl di-hydrogenated tallow ammonium monopersulfate.

**EXAMPLE 8**

The bleaching effect of dimethyl di-hydrogenated tallow ammonium monopersulfate (DDTAM), produced by the method set forth in Example 7, was compared with a standard bleaching agent, potassium monopersulfate, using the following procedure: Thirty-two cotton swatches (5" x 5" desized cotton Indianhead fabric, uniform in weave and thread count) were stained with tea. The staining was accomplished by placing 5 tea bags in a liter of water and boiling for 5 minutes, and thereafter immersing the swatches in the tea and continuing the boiling for an additional 5 minutes. The stained swatches were then squeezed to remove excess fluid, dried, rinsed in cold water and dried.

Three of the stained cotton swatches were added to each of a series of stainless steel Terg-O-Tometer vessels (produced by the U.S. Testing Company) containing 1,000 ml. of a 0.2% standard detergent solution at a temperature of 120° F. Measured amounts of each of the bleaches were then added to separate vessels sufficient to correspond to predetermined active oxygen contents. The pH of the solutions in the vessels were adjusted to 9.5 using soda ash. Cut-up pieces of white terry cloth toweling were added to provide a typical household wash water/cloth ratio of 20:1. The Terg-O-Tometer was then operated at 72 cycles per minute for 15 minutes at a temperature of 120° F. At the end of the wash cycle, the swatches were removed, rinsed under cold tap water and dried in a Proctor-Schwarz skin dryer. The tests were run in triplicate and include detergent blanks. Reflectance readings of the swatches were taken before and after the wash cycle with a Hunter model D-40 Reflectometer using the blue filter. Each swatch was read twice (warp and fill) on either side, with a backing of 5 similarly soiled swatches. Fluorescent effect was excluded in all readings. The resultant reflectance increase over blank samples at various active oxygen concentrations is given in the drawing for both the DDTAM and the potassium peroxydisulfate.

**EXAMPLE 9**

The softening effect of dimethyl di-hydrogenated tallow ammonium monoperoxysulfate (DDTAM), produced by the method set forth in Example 7, was tested by the method set forth in ASTM D1175-55T. This test measures the number of standard flex abrasion cycles a cloth can withstand before being abraded. The test was carried out as follows: Cotton samples having thread counts of 80 x 80 and 136 x 64, and a Dacron sample were placed in a domestic washing machine and run through a domestic washing machine with a standard detergent. In the final rinse 4.72 grams of DDTAM (100% active material) were added to the 18 gallons of wash water. The total solids load was 7.5 pounds of (dry) cloth. This permitted the solution to deposit on each cloth 0.1375% softer solids based on the weight of the cloth. A duplicate blank was also run in which no softener was added to the cloth. The samples thus treated were placed on the flex abrasion tester and the number of abrasion cycles was recorded before the cloth was abraded. The results of the tests are shown in Table I.

**TABLE I**

<table>
<thead>
<tr>
<th>Sample Material</th>
<th>Abrasion Cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>DDTAM</td>
<td>Blank</td>
</tr>
<tr>
<td>90 x 80 cotton cloth</td>
<td>681</td>
</tr>
<tr>
<td>136 x 64 cotton cloth</td>
<td>1,235</td>
</tr>
<tr>
<td>Dacron</td>
<td>50,110</td>
</tr>
</tbody>
</table>

Softening of the cloth is indicated by the increase in abrasion cycles required to abrade the cloth. The greater the softer action, the greater the increase in abrasion cycles required.

**EXAMPLE 10**

The procedure used in Example 7 was repeated except that the reagents used were 11.8 g. of Arquad 16 and 4.5 g. of potassium monopersulfate. Arquad 16 is a proprietary solution containing 50% by weight of palmityl-trimethyl ammonium chloride. The resultant white solid product weighed 5.8 g. and had an active oxygen content of 3.05% by weight. It was identified as palmityl-trimethyl ammonium monoperoxysulfate.

**EXAMPLE 11**

The procedure of Example 7 was repeated except that the reagents employed were 13.9 g. of Arquad 18 and 4.5 g. of potassium monopersulfate. The resultant white solid product weighed 5.8 g. and had an active oxygen content of 3.01% by weight. The product was identified as stearyl-trimethyl ammonium monoperoxysulfate.

**EXAMPLE 12**

The procedure of Example 7 was repeated except that the reagents employed were 23.5 g. of Aliquot 207 and 6.0 g. of potassium monopersulfate. The resultant white solid product weighed 20 g. and had an active oxygen content of 2.02% by weight. The product was identified as distearyldimethyl ammonium monoperoxysulfate.

Persuant to the requirements of the patent statute, the principle of this invention has been explained and exemplified in a manner so that it can be readily practiced by those skilled in the art, such exemplification including what is considered to represent the best embodiment of the invention. However, it should be clearly understood that the invention may be practiced by those skilled in the art, and having the benefit of this disclosure otherwise than as specifically described and exemplified herein.

What is claimed is:

1. A compound having the formula:

   \[
   R_1 (B_1N_1 - R_2)HSO_4
   \]

   wherein \(R_1\) and \(R_3\) are selected from the group consisting of ethyl and methyl and \(R_2\) and \(R_4\) are selected from the class consisting of:

   (1) alkyl, cycloalkyl and substituted alkyl and cycloalkyl groups having up to 18 carbon atoms wherein the substituents are selected from the group consisting of carboxyl, alkoxy, amido, nitro and phenyl, and

   (2) phenyl and substituted phenyl groups having up to 18 carbon atoms wherein the substituents are selected from the group consisting of carboxyl, alkoxy, amido, nitro, halogen and alkyl.

2. A compound having the formula:

   \[
   R_1 (B_1N_1 - R_2)HSO_4
   \]

   wherein \(R_1\) and \(R_3\) are selected from the group consisting of ethyl and methyl and \(R_2\) and \(R_4\) are alkyl groups having up to 18 carbon atoms.

3. The compound of claim 1 wherein at least one of the said \(R_2\) and \(R_4\) groups has from 12 to 18 carbon atoms.
4. The compound dimethyl di-hydrogenated tallow ammonium monoperoxysulfate.

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<tbody>
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<td>812,752 4/1959 Great Britain</td>
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CHARLES B. PARKER, Primary Examiner
S. T. LAWRENCE III, Assistant Examiner
U.S. Cl. X.R.
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Inventor(s) Louis H. Diamond and John H. Blumbergs

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

Column 1, line 16, "fabric" should read --fabrics--.
Column 2, line 12, "S₂O₅" should read --S₂O₈--.
Column 2, line 46, "K₂S₂O₅" should read --K₂S₂O₈--.
Column 2, line 46, "S₂O₅" should read --S₂O₈--.
Column 2, line 46, should be a bracket in front of R₂-N-R₄.
Column 3, line 23, "produce" should read --product--.
Column 6, line 52, "C₁₀" should read --C₁₈--.

Attest:
Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents