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3,332,882

PEROXYGEN COMPOSITIONS

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13 Claims. (Cl. 252—186)

This application is a continuation-in-part of Ser. No. 419,582 filed on Dec. 18, 1964, in the names of John H. Blumbergs, Donald G. MacKellar and Sidney Berkowitz, now abandoned.

This invention relates to peroxygen compositions and preferably to the activation of those peroxygen compositions which contain a solid peroxygen compound to provide the bleaching, disinfecting and sanitizing action.

In the make-up of granular laundering compositions, it is desired to add a solid bleaching agent to the formulation in order to obtain bleaching simultaneously with cleaning. The solid bleaching agent ideally must be one which is stable at room temperature, thereby assuring good shelf life, but which is capable of bleaching at the temperatures normally employed in domestic washing machines. One class of compounds which approaches these requirements is the solid peroxygen compounds such as the alkali perborates. The difficulty with these solid bleaching agents is that they do not bleach effectively until boiling temperatures are employed. Since the temperature of the water in domestic washing machines does not normally rise above about 80° C., the full bleaching effect of the peroxygen compound is not obtained.

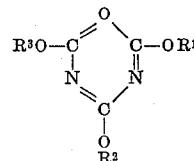
In an effort to solve this difficulty, many "activators" have been suggested in the prior art in order to permit the active oxygen compounds, e.g., perborates, to bleach effectively at lower temperatures. Many such activators have been suggested, such as esters of phenol or substituted phenols (U.S. Patent 3,130,165, issued Apr. 12, 1964, to Peter Brocklehurst) and N-acylimides (U.S. Patent 3,061,550, issued Oct. 30, 1962, to Melvin Myron Baevsky). While these activators have been found somewhat effective, the small degree of activation obtained leaves much to be desired. As a result there is a need for a more effective activator than those presently employed in the art so that better bleaching can be obtained with these solid peroxygen bleaching compounds.

It is an object of the present invention to incorporate an activator in compositions containing peroxygen compounds in order to enhance the bleaching, disinfecting and sanitizing powers of these compositions when used in aqueous solutions at temperatures below boiling.

This and other objects will be apparent from the following description.

We have now found that peroxygen compounds, including solid peroxygen compounds and hydrogen peroxide, can be activated to bleach, disinfect and sanitize more effectively when used in aqueous solutions at temperatures below boiling by incorporation of an aromatic or lower aliphatic acyl derivative of 2,4,6-trihydroxy-1,3,5-triazine. These compounds have the general formula:

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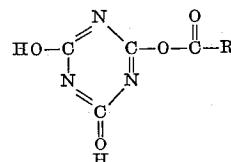


where at least one of R¹, R², or R³ are acyl groups having the formula:



wherein R is either hydrogen, an aromatic group of an aliphatic group having from 1 to 6 carbon atoms, and any remaining R¹, R² or R³ groups are hydrogen. The acyl derivative must be soluble in the bleach solution in amounts of at least about 100 p.p.m. to be effective.

The monoacyl derivative has the formula:



where R may be hydrogen, an aromatic grouping, or an aliphatic group having from 1 to 6 carbon atoms. The diacyl and triacyl derivatives are identical to the monoacyl structure shown above except that additional acyl groupings are added to the cyclic structure by acylating one or both of the remaining hydroxyl groups.

In practicing the present invention for making up detergent mixtures, the solid peroxygen compound is mixed together with a phosphate builder such as sodium tripolyphosphate in combination with one or more working ingredients. These include antiredeposition agents such as sodium carboxymethylcellulose, anionic or nonionic surfactants and anticorrosion agents such as sodium silicate.

The activator is added to mixture, preferably in an amount sufficient to have at least one acyl group present for every atom of available oxygen. Obviously, larger amounts of the activator can be used to assure complete activation of the peroxygen compound. Also, smaller amounts of the activator can be used to assure complete controlled bleaching effect is desired. The solid peroxygen compound is employed in amounts sufficient to achieve the desired degree of bleaching. For home bleaching applications amounts sufficient to supply from about 10 to about 100 p.p.m. of active oxygen normally are employed in the wash solution. A preferred amount is about 40 p.p.m.

In the make-up of the final bleaching mixture it is desirable to keep the solid peroxygen compound and the activator out of contact with one another until placed in the wash water to avoid any possible reaction between these ingredients, even in the dry state. This can be done most readily when making up a single mixture by coating the activator with a water soluble coating prior to mixing it with the remaining components of the bleaching mix. In this way the activator and the solid peroxygen compound can be mixed together and still remain out

of contact with one another until the mixture is placed in the wash water. Another alternative is to separately package the solid peroxygen compound and the activator so that they are physically out of contact with one another in the consumer package.

The solid peroxygen compounds which are useful in the present process as bleaching, disinfecting or sanitizing agents are those which liberate perhydroxyl anions readily when dissolved in an aqueous media. These include the alkali perborates such as sodium perborate and other alkali metal percompounds such as percarbonates, persilicates, perphosphates, and perpyrophosphates. In addition, such compounds as sodium peroxide, zinc peroxide, calcium peroxide, magnesium peroxide, urea peroxide, and others are included within the term solid peroxygen compound.

In the practice of the present invention with peroxygen compounds such as hydrogen peroxide, the article to be treated is contacted with an aqueous solution containing the peroxygen compound, e.g., H_2O_2 , and the present activator at ambient temperatures or above as desired. This is effective in bleaching wood pulp, commercial textiles, fats, oils and all common materials and compounds that are traditionally bleached with solutions of hydrogen peroxide. These aqueous solutions of the peroxygen compounds and the activator can also be used in sanitizing and disinfecting applications as well as for bleaching. The amount of peroxide utilized will vary with the specific material being treated. For example, the bleaching of fats or oils may require greater concentrations of peroxide, than textile bleaching, to achieve the desired whiteness. The present activator is added, preferably in amounts sufficient to have up to about one acyl group present for every atom of available active oxygen, regardless of the quantity of peroxygen compound utilized in the treating solution.

The acyl moieties of the present activators have the formula:



in which R can be an aromatic group, i.e., a phenyl group, or an aliphatic group containing up to 6 carbon atoms in which the aliphatic group can be cyclic or acyclic. The aromatic or aliphatic R groups may be substituted with any functional substituents that are not oxidized by the peroxygen compound in solution. Examples of substituents that are acceptable are the halogens such as chlorine or bromine, phenyl groups, nitro groups, carboxy groups, and the like. Examples of substituents that are not acceptable because they are subject to oxidation include unsaturated groups such as vinyls, amino, imino, sulphydryl, hydroxy, and sulfides.

The present activators can be made by the general process of J. Ponomarew reported in Ber. 18, 3261 (1885). Suitable activators include the mono-, di-, and tri-acetyl derivatives of 2,4,6-trihydroxy-1,3,5-triazine; the mono- and di-benzoyl derivatives of 2,4,6-trihydroxy-1,3,5-triazine; the mono- and dicyclohexanoyl derivatives of 2,4,6-trihydroxy-1,3,5-triazine; and the mono- and di-propionyl derivatives of 2,4,6-trihydroxy-1,3,5-triazine. The preferred derivatives are the nonsubstituted derivatives because they are easier to prepare and are more effective per unit weight than the substituted derivatives.

The following examples are given to illustrate the present invention and are not deemed to be limiting thereof.

Example 1

Bleaching tests were carried out by bleaching tea, coffee and wine stained cotton swatches (5" x 5") with sodium perborate tetrahydrate alone and in the presence of various activators. The procedure used was as follows: 32 cotton swatches (5" x 5" desized cotton Indianhead fabric, 48 fill by 48 warps threads per inch, uniform in weave and thread count) were stained with tea, coffee and wine in the following manner. Five tea bags were placed in a

liter of water and boiled for 5 minutes. Thereafter, the swatches were immersed in the tea and the boiling continued for 5 minutes. Thirty-two additional swatches of the same cloth were coffee stained by boiling 50 g. of coffee in a liter of water, immersing the swatches in the coffee solution, and boiling for an additional 5 minutes. The wine stains were created by soaking swatches of the same cloth in a red wine at room temperature. The stained swatches were then squeezed to remove excess fluid, dried, rinsed in cold water, and dried. Three of the stained cotton swatches were then added to each of a series of stainless steel Terg-o-Tometer vessels (produced by the U.S. Testing Company) containing 1000 ml. of a 0.2% standard detergent solution at a temperature of 120° F. Measured amounts of sodium perborate tetrahydrate bleach were then added to each vessel sufficient to correspond to an active oxygen content of 60 p.p.m. The pH of the solutions was adjusted to 9.0 using soda ash. Cut up pieces of white terry cloth toweling were then added to provide a typical household wash water: cloth ratio of 20:1. The activators specified in Table I were then added to the solution in the ratio set forth in Table I. 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-Schwartz skein dryer. The tests were run in triplicate and included detergent blanks. Reflectance readings of the swatches were then taken before and after the wash cycle with a Hunter Model D-40 Reflectometer and the readings were averaged. The percent stain removal was obtained according to the following formula:

$$\text{Percent stain removal} =$$

$$\frac{\text{reflectance after bleaching} - \text{reflectance before bleaching}}{\text{reflectance before staining} - \text{reflectance stained}} \times 100$$

The results are reported in Table I below.

TABLE I

| Activator Added | Ratio Activator/Perborate by Wt. | Percent Stain Removal | | |
|---------------------------------------------------------|----------------------------------|-----------------------|--------|------|
| | | Tea | Coffee | Wine |
| None | | | | |
| Detergent blank | | 26.9 | 45.0 | 61.0 |
| None | | | | |
| Perborate blank | | 33.2 | 51.2 | 69.4 |
| Diacetyl derivative of 2,4,6-trihydroxy-1,3,5-triazine | 1/1 | 62.4 | 88.6 | 82.7 |
| Triacetyl derivative of 2,4,6-trihydroxy-1,3,5-triazine | 0.8/1 | 63.0 | 89.2 | 96.0 |
| Dibenzoyl derivative of 2,4,6-trihydroxy-1,3,5-triazine | 1.2/1 | 61.4 | 90.0 | 88.0 |

Example 2

The procedure of Example 1 was repeated using sodium perborate tetrahydrate as the solid peroxygen compound except that the sodium perborate tetrahydrate was added in amounts to supply only 40 p.p.m. of active oxygen instead of the 60 p.p.m. active oxygen used in Example 1. The activator added was the triacetyl derivative of 2,4,6-trihydroxy-1,3,5-triazine and was added in the amounts specified in Table II. The results of the test are reported in Table II below.

TABLE II

| Activator Added | Ratio Activator/Perborate by Wt. | Percent Stain Removal | | |
|---------------------------------------------------------|----------------------------------|-----------------------|--------|------|
| | | Tea | Coffee | Wine |
| None | | | | |
| Perborate blank | | 26.7 | 55.0 | 60.9 |
| Triacetyl derivative of 2,4,6-trihydroxy-1,3,5-triazine | 0.8/1 | 60.8 | 83.7 | 82.0 |

Example 3

The same procedure was employed as in Example 2, except that the sodium perborate tetrahydrate was replaced with sodium pyrophosphate peroxyhydrate in amounts to supply 40 p.p.m. active oxygen in the bleaching solution. The results are reported in Table III.

TABLE III

| Activator Added | Ratio Activator/ Sodium Pyrophos- phate Per- oxyhydrate by Wt. | Percent Stain Removal | | |
|-------------------------------------------------------------|----------------------------------------------------------------------------------|-----------------------|--------|------|
| | | Tea | Coffee | Wine |
| None | | | | |
| Sodium Pyrophosphate Per- oxyhydrate blank | | 28.0 | 52.0 | 60.3 |
| Triacetyl derivative of 2,4,6- trihydroxy-1,3,5-triazine | 0.75/1 | 61.3 | 82.8 | 84.0 |

Example 4

The same procedure was employed as in Example 2, except that the sodium perborate tetrahydrate was replaced with hydrogen peroxide in amounts to supply 40 p.p.m. of active oxygen in the bleaching solution. The pH was adjusted to 9.0 by adding soda ash. The results of the test are reported in Table IV.

TABLE IV

| Activator Added | Ratio Activator/ Hydrogen Peroxide by Wt. | Percent Stain Removal | | |
|---------------------------------------------------------|-------------------------------------------------------|-----------------------|--------|------|
| | | Tea | Coffee | Wine |
| None | | | | |
| Hydrogen Peroxide blank | | 27.0 | 54.2 | 61.3 |
| Triacetyl derivative of 2,4,6-trihydroxy-1,3,5-triazine | 3.8/1 | 62.0 | 84.0 | 85.0 |

Example 5

The same procedure was employed as in Example 2 using the various ratios of the activator to sodium perborate tetrahydrate reported in Table V. The total active oxygen in the bleaching solution was 60 p.p.m. In this experiment only tea stained cotton swatches were bleached. The results of the test are reported in Table V.

TABLE V

| Activator Added | Ratio Activator/ Perborate by Wt. | Percent Stain Removal, Tea |
|--------------------------------------------------------------|--------------------------------------------|-------------------------------|
| None..... | | 31. |
| Perborate blank..... | | |
| Triacetyl derivative of 2,4,6-trihydroxy-1,3,5-triazine..... | 1/1 | 71. |
| Do..... | 0.8/1 | 67. |
| Do..... | 0.67/1 | 64. |
| Do..... | 0.5/1 | 59. |

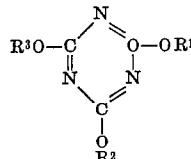
In general, the peroxygen compound and the activator can be used in any application in which the peroxygen compound is useful per se. Thus, in addition to bleaching, disinfecting and sanitizing applications, the present activated peroxygen compounds are useful as polymerization catalysts in the polymerization of butadiene-styrene or acyclic polymers and the like. Other common applications for these activated peroxygen compounds will be readily apparent to those skilled in the art.

Pursuant to the requirements of the patent statutes, 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, within the scope of the appended claims, the invention

tion 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:

5 1. A process for activating a peroxygen bleaching compound selected from the group consisting of alkali metal perborates, alkali metal percarbonates, alkali metal persilicates, alkali metal perphosphates, alkali metal perpyrophosphates, sodium peroxide, zinc peroxide, calcium peroxide, magnesium peroxide, urea peroxide and hydrogen peroxide in an aqueous bleaching solution which comprises adding an activator having the general formula:



where at least one of R^1 , R^2 and R^3 are acyl groups having the formula:



in which R is selected from the class consisting of hydrogen, an aryl group, alkyl and cycloalkyl groups having from 1 to 6 carbon atoms, any remaining R¹, R² and R³ groups being hydrogen, said activator being soluble in said aqueous bleaching solution in amounts of at least 100 p.p.m., said activator being present, relative to said peroxygen bleaching compound, in amounts sufficient to have at least about one acyl group present per atom of available oxygen in said peroxygen bleaching compound.

35 available oxygen in said peroxygen bleaching compound.

2. Process of claim 1 wherein said aqueous bleaching solution is used to bleach textiles.

3. Process of claim 1 in which the bleaching compound is sodium perborate.

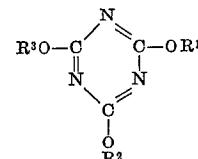
40 4. Process of claim 1 in which the bleaching compound is hydrogen peroxide.

5. Process of claim 1 in which the peroxygen bleaching compound is an alkali metal perborate.

6. Process of claim 1 in which the activator is the tri-acetyl derivative of 2,4,6-trihydroxy-1,3,5-triazine.

45 7. Process of claim 1 in which the activator is the dibenzoyl derivative of 2,4,6-trihydroxy-1,3,5-triazine.

8. A composition consisting essentially of a peroxygen compound selected from the group consisting of alkali metal perborates, alkali metal percarbonates, alkali metal persilicates, alkali metal perphosphates, alkali metal perpyrophosphates, sodium peroxide, zinc peroxide, calcium peroxide, magnesium peroxide, urea peroxide and hydrogen peroxide and an activator having the general formula:



where at least one of R^1 , R^2 and R^3 are acyl groups having the formula:



in which R is selected from the class consisting of hydrogen, an aryl group, alkyl and cycloalkyl groups having from 1 to 6 carbon atoms, any remaining R¹, R² and R³ being the same or different and each being a hydrocarbon group having from 1 to 6 carbon atoms.

70 groups being hydrogen, said activator being soluble in an aqueous treating solution in amounts of at least about 100 p.p.m., said activator being present, relative to said peroxygen compound, in amounts sufficient to have at least about one acyl group present per atom of available 75 oxygen in said peroxygen compound.

9. Composition of claim 8 in which the peroxygen compound is an alkali metal perborate.

10. Composition of claim 8 in which the activator is the triacetyl derivative of 2,4,6-trihydroxy-1,3,5-triazine.

11. Composition of claim 8 in which the activator is the dibenzoyl derivative of 2,4,6-trihydroxy-1,3,5-triazine.

12. Process of claim 8 in which said peroxygen compound is sodium perborate.

13. Process of claim 8 in which the peroxygen compound is hydrogen peroxide.

No references cited.

LEON D. ROSDOL, *Primary Examiner.*

I. GLUCK, *Assistant Examiner.*

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

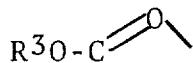
Patent No. 3,332,882

July 25, 1967

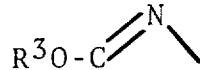
John H. Blumbergs et al.

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

Column 2, lines 1 to 8, for that portion of the formula reading



read



same column 2, lines 49 and 50, for "used to assure complete controlled" read -- employed where a controlled --; column 3, line 62, for "area" read -- are --.

Signed and sealed this 29th day of October 1968.

(SEAL)

Attest:

Edward M. Fletcher, Jr.

Attesting Officer

EDWARD J. BRENNER

Commissioner of Patents