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(54) **Mixed peroxyacid bleaches having improved bleaching power.**

(57) A dry laundry bleach composition comprising a mixture of peroxyacids provides enhanced bleaching of «real world» soils. The compositions of this invention comprise at least two bleaches selected from different classes of peroxyacids. A preferred composition comprises perlauric acid, a hydrophobic bleach and diperoxydodecanedioic acid, a hydrotropic bleach.

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MIXED PEROXYACID BLEACHES HAVING IMPROVED BLEACHING POWER

0068547

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TECHNICAL FIELD

This invention relates broadly to bleaching compositions. More particularly, this invention relates to bleaching compositions which derive their bleaching activity from a compound having an active oxygen content. Still more particularly, this invention relates to peroxyacid bleaching compositions.

BACKGROUND ART

Many compounds which have oxidative bleaching activity are well known in the art. Among these are the diperoxyacids, monoperoxyacids, perborates, hydrogen peroxide, sodium peroxide, organic peroxides, dichromates and certain chlorine-containing compounds such as sodium hypochlorite, sodium chlorite and chlorine dioxide. Such compounds are not always satisfactory for any given bleaching application, however. Some are frequently characterized by insufficient or excessive bleaching action under certain conditions and they are frequently characterized by insufficient bleaching action for certain types of soils or stains.

Peroxygen bleaching agents in general and peroxyacid compounds in particular have long been recognized as effective bleaching agents for use when the adverse color

and fabric damage effects of harsh active halogen bleaching agents cannot be tolerated. See, for example, Canadian Pat. No. 635,620, issued January 30, 1962, to McCune. U.S. Pat. No. 3,414,593, issued December 3, 1968, to Robson, discloses alpha-sulfo peroxy fatty acid compounds as detergents and bleaching agents.

Utilization of peroxyacid materials in commercial bleaching products, however, posed several problems. Liquid bleaching compositions containing peroxyacid materials as the active bleaching agent have the tendency to diminish in bleaching effectiveness over prolonged storage periods. Likewise, granular bleaching products containing peroxyacid compounds also tended to lose bleaching activity during storage, as well as pose a safety problem due to their exothermic decomposition properties. Dry peroxyacid compositions having improved exotherm control are disclosed in U.S. Pat. No. 4,100,095, issued July 11, 1978, to J. P. Hutchins.

Peroxyacid bleach compositions having increased solubility are also disclosed in U.S. Pat. No. 4,126,573, November 21, 1978, to Johnston.

Johnston discovered that the solubility of solid peroxyacids can be maintained by coating the peroxyacid particles with a surfactant compound and thereby maintain bleach effectiveness and fabric safety over an extended shelf life.

Two early patents of interest are: U.S. Pat. Nos. 1,687,803 and 1,687,804, October 16, 1928, both to Stoddard et al., which relate to mixtures of bleaches for bleaching foodstuffs, soaps, waxes and the like, particularly flour, cottonseed, seed meals, egg yolks oils and fats. These patents disclose that "peroxids or per acids of fatty acids, notably peroxids of higher or so-called soap forming

fatty acids" act as "activators" for liquid or semi-liquid organic peroxides such as benzoyl peroxides. U.S. Pat. 1,687,804 discloses that inorganic and organic peroxide which has a high proportion of available oxygen but an ordinarily low efficacy as a bleach may be activated by the addition of 1-20% of an organic peroxide which is a more active bleach. The preferred activating organic peroxyacids are the fatty acids.

In accordance with the present invention, it has been discovered that hydrophilic peroxyacid bleaches are effective bleaches for hydrophilic soils, but ineffective for bleaching hydrophobic soils, and vice versa, hydrophobic peroxyacid bleaches are more effective on hydrophobic soils. Yet other peroxyacid bleaches, hydrotropic, are somewhere in between the hydrophilic and hydrophobic bleaches in effectiveness on a particular type of soil. Bleaching ineffectiveness on a particular type of soil equates with poorer overall bleaching. This problem has not been recognized and addressed in modern peroxyacid bleach art.

In typical laundry loads, fabrics contain both hydrophilic and hydrophobic stains.

It is an object of the present invention to provide mixtures of peroxyacids which have enhanced bleaching for "real world soils" laundering situations involving both hydrophilic and hydrophobic soils.

Other objects of the present invention will be apparent in the light of the following disclosure.

SUMMARY OF THE INVENTION

The present invention is directed to a laundry bleach comprising a mixture of peroxyacid bleaches selected from the group consisting of:

a + b, a + c, b + c, a + (b + c), b + (a + c), c + (a + b)

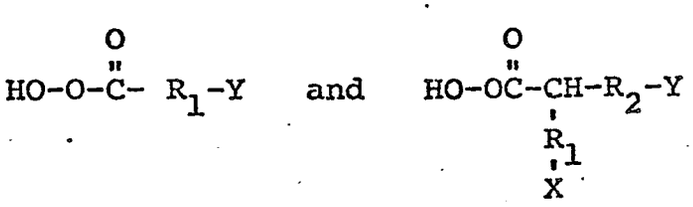
wherein "a" is a hydrophilic bleach, "b" is a hydrotropic

bleach, and "c" is a hydrophobic bleach, and wherein said peroxyacid bleaches in said mixture are in a ratio of a/b, a/c, b/c, a/(b+c), b/(a+c), or c/(a+b) of from 1:20 to 20:1 on a parts per million (ppm) available oxygen basis. The "hydrophilic" peroxyacid bleach of the present invention is a bleach whose parent carboxylic acid or salt thereof has no measurable critical micelle concentration (CMC) below 0.5 moles per liter and a high pressure liquid chromatographic retention time of less than 5 minutes under the conditions as described herein. The "hydrotropic" bleach is one whose parent carboxylic acid has no measurable CMC below 0.5M and has a high pressure liquid chromatographic retention time of greater than 5 minutes, and the "hydrophobic" bleach is one whose parent carboxylic acid has a measurable CMC of less than 0.5M. In accordance with the present invention, the CMC is measured in aqueous solution at 20°-50°C.

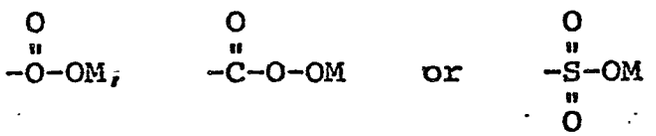
DETAILED DESCRIPTION OF THE INVENTION

The two essential components of the present invention are at least two peroxyacid compounds selected from different classes of peroxyacids. These will be described in turn below.

The peroxyacid bleach composition of the instant invention comprises a mixture of at least two peroxyacid compounds. The preferred peroxyacid compounds are "normally solid", i.e., dry or solid at room temperature. The peroxyacid compounds of the present invention, in general, are the organic peroxyacids, water-soluble salts thereof which yield a species containing a $-O-O^-$ moiety in aqueous solution, and adducts of the organic peroxyacids and urea. These materials have the general formulae:



wherein R_1 and R_2 are alkylene groups containing from 1 to about 20 carbon atoms or phenylene groups, and X and Y are hydrogen, halogen, alkyl, aryl or any group which provides an anionic moiety in aqueous solution. Such X and Y groups can include, for example,



wherein M is H or a water-soluble, salt-forming cation. It is preferred that the acids used in the present invention be dried to a moisture level lower than 1.0%, and preferably lower than 0.5%.

Herein, peroxyacids are classified as either (1) hydrophilic, (2) hydrophobic, or (3) hydrotropic. These classifications are based on their different levels of effectiveness on real world soils. Real world soils contain hydrophilic and/or hydrophobic components. A hydrophilic bleach is most effective on a hydrophilic bleachable soil, such as tea (tannic acid based), fruit juices, and the like. On the other hand, hydrophobic bleaches are most effective on hydrophobic bleachable soils, such as body soils (fatty acid/triglyceride based). Hydrotropic bleaches find utility on both types of soils, but are less effective on hydrophilic soils than hydrophilic bleaches and less effective on hydrophobic soils than hydrophobic bleaches. Combinations of peroxyacids of the different classes result in better overall bleaching than is achieved with a single peroxyacid.

The "hydrophilic bleach" is defined as a peroxyacid whose parent carboxylic acid (or the salts thereof): (1) has no measurable critical micelle concentration (CMC) below 0.5 moles per liter (M/l) and (2) has a chromatographic retention time of less than 5.0 minutes under the

following high pressure liquid chromatographic (HPLC) conditions:

Elution with 50:50 methanol/water solvent at the rate of 1.5 ml/min. through a DuPont Zorbax ODS® column using a Waters R-401 Refractive Index Detector®.

The "hydrophobic bleach" is defined as a peroxyacid whose parent carboxylic acid (or salts thereof) has a CMC of less than 0.5M.

The "hydrotropic bleach" is defined as a peroxyacid whose parent carboxylic acid (or salts thereof) has no measurable CMC below 0.5M and has a chromatographic retention time of greater than 5.0 minutes under the HPLC conditions described above. In accordance with the present invention, the CMC is measured in aqueous solution at 20°-50°C.

Examples of the three classes of peroxyacid bleaches are as follows:

Class a - Hydrophilic peroxyacid bleaches can include:

1. Alkyl alpha, omega - diperoxyacids

$HO_3C-(CH_2)_n-CO_3H$ n = 2-7, preferably 2-5;

e.g., diperoxyadipic acid wherein n = 4.

2. Alkyl monoperoxydioic acids

$HO_2C-(CH_2)_n-CO_3H$ n = 2-7, preferably 2-5;

e.g., monoperoxyadipic acid wherein n = 4.

3. Alkyl monoperoxyacids

$CH_3-(CH_2)_nCO_3H$ n = 0-5, preferably 0-3;

e.g., peroxybutyric acid wherein n = 2.

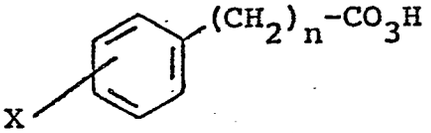
4. Alpha-substituted monoperoxyacids

$$CH_3(CH_2)_n-\underset{X}{CH}-CO_3H$$

n = 0-5, preferably 0-3; X = CH_2CO_2H, $-CH_2CO_3H$, $-SO_3Na^+$, or $-N^+R_1R_2R_3$ and wherein any R = H or C_1-C_4;

e.g., peroxypentanoic acid, 2-propyl monoperoxysuccinic acid, diperoxysuccinic acid, alpha-sulfoperoxypentanoic acid and alpha-tetramethylammonium peroxypentanoic acid, respectively, wherein n = 2.

5. Aromatic monoperoxyacids



X: substitution in 2-6 position

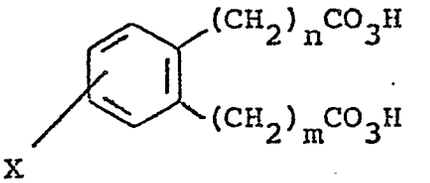
n = 0-6, preferably 0-3;

X = Hydrogen, Halogen, $-(CH_2)_mCO_2H$ or Aromatic;

m = 0-7 and n+m = 0-7;

e.g., peroxybenzoic acid wherein n = 0 and X = Hydrogen.

6. Aromatic diperoxyacids



X and $-(CH_2)_mCO_3H$: substitution in 2-6 position

X = Hydrogen, Halogen or Aromatic

n+m = 0-7, preferably 0-4;

e.g., diperoxyphthalic acid wherein n = m = 0 and X = Hydrogen.

Class b - Hydrotropic peroxyacid bleaches can include:

1. Alkyl alpha, omega - diperoxyacids

$HO_3C-(CH_2)_n-CO_3H$ n = 8-14, preferably 9-12;

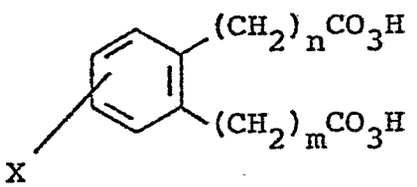
e.g., diperoxydodecanedioic acid wherein n = 10.

2. Alkyl monoperoxydioic acids

$HO_2C-(CH_2)_n-CO_3H$ n = 8-14, preferably 9-12;

e.g., monoperoxydodecanedioic acid.

3. Aromatic diperoxyacids



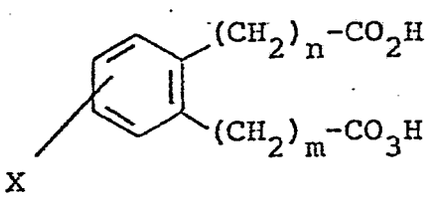
X and $-(CH_2)_mCO_3H$: substitution in 2-6 position

X = Hydrogen, Halogen or Aromatic

n+m = 8-14, preferably 9-12;

e.g., 1,2-(5-peroxypentanoic acid)benzene wherein m = n = 5 and X = Hydrogen.

4. Aromatic monoperoxydioic acids



X and $-(CH_2)_mCO_3H$: substitution in 2-6 position

X = Hydrogen, Halogen or Aromatic

n+m = 8-14, preferably 10-14;

e.g., 1-(5-pentanoic acid)-2-(5-peroxypentanoic acid)benzene wherein m = n = 5 and X = Hydrogen.

Class c - Hydrophobic peroxyacid bleaches can include:

1. Alkyl monoperoxyacids

$CH_3(CH_2)_n-CO_3H$ n = 6-16, preferably 8-12;

e.g., peroxylauric acid wherein n = 10.

For example, C_8-C_{16} monoperoxyacids belong to the hydrophobic class since the CMC of each parent acid is less than 0.5M. (Table I-A)

2. Alpha-substituted alkyl monoperoxyacids

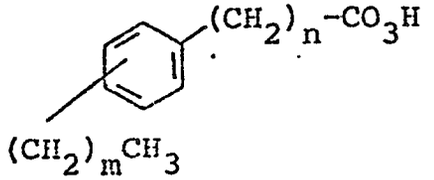
$$CH_3-(CH_2)_n-\underset{X}{CH}-CO_3H$$

n = 6-16, preferably 8-16; X = $-CH_2CO_2H$, $-CH_2CO_3H$, $-SO_3Na^+$, or $-N^+R_1R_2R_3$ and

R = Hydrogen or C_1-C_{16};

e.g., 2-lauryl monoperoxysuccinic acid wherein n = 11; 2-lauryl diperoxysuccinic acid wherein n = 11; alpha-sulfo hexadecanoic acid wherein n = 13; and alpha-tetramethylammonium hexadecanoic acid wherein n = 13 and the R's = CH_3.

3. Aromatic peroxyacids



substitution in 3-5 position

m = 8-16, preferably 10-16;

n = 0-16;

e.g., 4-lauryl peroxybenzoic acid.

TABLE I-A

Typical Critical Micelle Concentrations[1] For The Sodium Salts of Carboxylic Acids

	Critical Micelle Concentration[2] (Molar)
Sodium octanoate	3.5×10^{-1}
Sodium decanoate	9.6×10^{-2}
Sodium dodecanoate	2.3×10^{-2}
Sodium tetradecanoate	6.9×10^{-3}
Sodium hexadecanoate[3]	2.1×10^{-3}

[1]Source: Critical Micelle Concentrations of Aqueous Surfactant Systems, NSRDS-NBS 36, 1971.

[2]25°C, aqueous solution.

[3]50°C, aqueous solution.

In accordance with the present invention, among the hydrophobic peroxyacid bleaches, it has been found that those which have a long hydrocarbon chain with the percarboxylate group at one end (e.g., perlauric acid) tend to be more effective (on an equal available oxygen basis) in the bleaching of hydrophobic stains from fabrics than those which are not constructed in this way, e.g., peroxybenzoic acid and diperoxydodecanedioic acid.

The long chain peroxyacids with the percarboxylate groups at one end have a structure similar to surface active agents (surfactants). It is believed that in a washing solution, their hydrophobic "tail" tends to be attached to the hydrophobic stains on the fabrics, thereby causing a localized increase in bleach concentration around the stain and thus resulting in increased efficiency in bleaching for a given concentration of active oxygen in the bleaching solution.

Optional Components

Surfactants

Because of the relatively poor dispersibility of some peroxyacid bleaches, the surface active peroxyacid bleaches, it is highly desirable that surfactants be present in the bleaching solutions in which the peroxyacids are used. Surfactants should generally be present in the bleaching solution at a level of at least 150 ppm. It is the usual practice to bleach fabrics in a laundering solution which contains a laundry detergent. Such detergents contain surfactants and are generally used at solution concentrations which provide more than 200 ppm surfactant to the solution. Thus, if the bleach compositions herein are to be used with a laundry detergent there is no need to incorporate a surfactant into the bleach composition.

If surfactants are incorporated into the bleach compositions herein they will generally be present at levels of from 0.5% to 60%, preferably from 20% to 30% of the composition. Examples of suitable surfactants are given below.

Water-soluble salts of the higher fatty acids, i.e., "soaps," are useful as the anionic surfactant herein. This class of surfactants includes ordinary alkali metal soaps such as the sodium, potassium, ammonium and alkanolammonium salts of higher fatty acids containing from 8 to 24 carbon atoms and preferably from 10 to 20 carbon atoms. Soaps can be made by direct saponification of fats and oils or by the neutralization of free fatty acids. Particularly useful are the sodium and potassium salts of the mixtures of fatty acids derived from coconut oil and tallow, i.e., sodium or potassium tallow and coconut soaps.

Another class of anionic surfactants includes water-soluble salts, particularly the alkali metal, ammonium and alkanolammonium salts, of organic sulfuric reaction

products having in their molecular structure an alkyl group containing from 8 to 22 carbon atoms and a sulfonic acid or sulfuric acid ester group. (Included in the term "alkyl" is the alkyl portion of acyl groups.) Examples of this group of synthetic surfactants which can be used in the present bleaching compositions are the sodium and potassium alkyl sulfates, especially those obtained by sulfating the higher alcohols (C_8-C_{18} carbon atoms) produced by reducing the glycerides of tallow or coconut oil; and sodium and potassium alkyl benzene sulfonates, in which the alkyl group contains from 9 to 15 carbon atoms in straight chain or branched chain configuration, e.g., those of the type described in U.S. Pat. Nos. 2,220,099, Guenther et al., issued November 5, 1940; and 2,477,383, Lewis, issued July 26, 1949.

Other anionic surfactant compounds useful herein include the sodium alkyl glyceryl ether sulfonates, especially those ethers of higher alcohols derived from tallow and coconut oil; sodium coconut oil fatty acid monoglyceride sulfonates and sulfates; and sodium or potassium salts of alkyl phenol ethylene oxide ether sulfates containing 1 to 10 units of ethylene oxide per molecule and wherein the alkyl groups contain 8 to 12 carbon atoms.

Other useful anionic surfactants herein include the water-soluble salts of esters of α-sulfonated fatty acids containing from 6 to 20 carbon atoms in the ester group; water-soluble salts of 2-acyloxy-alkane-1-sulfonic acids containing from 2 to 9 carbon atoms in the acyl group and from 9 to 23 carbon atoms in the alkane moiety; alkyl ether sulfates containing from 10 to 20 carbon atoms in the alkyl group and from 1 to 30 moles of ethylene oxide; water-soluble salts of olefin sulfonates containing from 12 to 24 carbon atoms; and β-alkyloxy alkane sulfonates

containing from 1 to 3 carbon atoms in the alkyl group and from 8 to 20 carbon atoms in the alkane moiety.

Preferred water-soluble anionic organic surfactants herein include linear alkyl benzene sulfonates containing from 11 to 14 carbon atoms in the alkyl group; the tallow range alkyl sulfates; the coconut range alkyl glyceryl sulfonates; and alkyl ether sulfates wherein the alkyl moiety contains from 14 to 18 carbon atoms and wherein the average degree of ethoxylation varies between 1 and 6.

Specific preferred anionic surfactants for use herein include: sodium linear C_{10}-C_{12} alkyl benzene sulfonate; triethanolamine C_{10}-C_{12} alkyl benzene sulfonate; sodium tallow alkyl sulfate; sodium coconut alkyl glyceryl ether sulfonate; and the sodium salt of a sulfated condensation product of tallow alcohol with from 3 to 10 moles of ethylene oxide.

It is to be recognized that any of the foregoing anionic surfactants can be used separately herein or as mixtures.

Nonionic surfactants include the water-soluble ethoxylates of C_{10}-C_{20} aliphatic alcohols and C_6-C_{12} alkyl phenols. Many nonionic surfactants are especially suitable for use as suds controlling agents in combination with anionic surfactants of the type disclosed herein.

Semi-polar surfactants useful herein include water-soluble amine oxides containing one alkyl moiety of from 10 to 28 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxylakyl groups containing from 1 to 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of 10 to 28 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from 1 to 3

carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from 10 to 28 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from 1 to 3 carbon atoms.

Ampholytic surfactants include derivatives of aliphatic amines or aliphatic derivatives of heterocyclic secondary and tertiary amines in which the aliphatic moiety can be straight chain or branched and wherein one of the aliphatic substituents contains from 8 to 18 carbon atoms and at least one aliphatic substituent contains an anionic water-solubilizing group.

Zwitterionic surfactants include derivatives of aliphatic quaternary ammonium, phosphonium and sulfonium compounds in which the aliphatic moieties can be straight or branched chain, and wherein one of the aliphatic substituents contains from 8 to 18 carbon atoms and one contains an anionic water-solubilizing group.

Detergency Builders

The instant granular compositions can also comprise those detergency builders commonly taught for use in laundry compositions. Useful builders herein include any of the conventional inorganic and organic water-soluble builder salts, as well as various water-insoluble and so-called "seeded" builders.

Inorganic detergency builders useful herein include, for example, water-soluble salts of phosphates, pyrophosphates, orthophosphates, polyphosphates, carbonates, bicarbonates, borates and silicates. Specific examples of inorganic phosphate builders include sodium and potassium tripolyphosphates, phosphates, and hexametaphosphates. Sodium tripolyphosphate is an especially preferred, water-soluble inorganic builder herein.

Nonphosphorus-containing sequestrants can also be selected for use herein as detergency builders. Specific

examples of nonphosphorus, inorganic builder ingredients include water-soluble inorganic carbonate, bicarbonate, borate and silicate salts. The alkali metal, e.g., sodium and potassium, carbonates, bicarbonates, borates (Borax) and silicates are particularly useful herein.

Water-soluble, organic builders are also useful herein. For example, the alkali metal, ammonium and substituted ammonium polyacetates, carboxylates, polycarboxylates, succinates, and polyhydroxysulfonates are useful builders in the present compositions and processes. Specific examples of the polyacetate and polycarboxylate builder salts include sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylene diamine tetraacetic acid, nitrilotriacetic acid, oxydisuccinic acid, mellitic acid, benzene polycarboxylic acids, and citric acid.

Highly preferred nonphsophorous builder materials (both organic and inorganic) herein include sodium carbonate, sodium bicarbonate, sodium silicate, sodium citrate, sodium oxydisuccinate, sodium mellitate, sodium nitrilotriacetate, and sodium ethylenediaminetetraacetate, and mixtures thereof.

Another type of detergency builder material useful in the present compositions comprises a water-soluble material capable of forming a water-insoluble reaction product with water hardness cations in combination with a crystallization seed which is capable of providing growth sites for said reaction product.

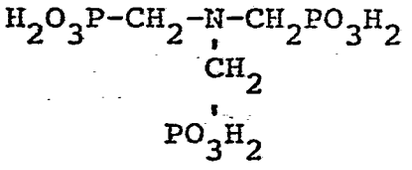
Specific examples of materials capable of forming the water-insoluble reaction product include the water-soluble salts of carbonates, bicarbonates, sesquicarbonates, silicates, aluminates and oxalates. The alkali metal, especially sodium, salts of the foregoing materials are preferred for convenience and ecomony.

Another type of builder useful herein includes various substantially water-insoluble materials which are capable of reducing the hardness content of laundering liquors, e.g., by ion-exchange processes. Examples of such builder materials include the phosphorylated cloths disclosed in U.S. Pat. No. 3,424,545, Bauman, issued January 28, 1969.

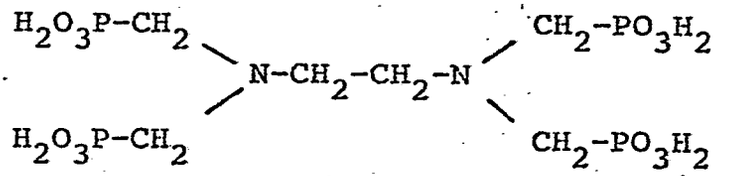
The complex aliminosilicates, i.e., zeolite-type materials, are useful detergency builders herein in that these materials soften water, i.e., remove hardness ions. Both the naturally occurring and synthetic "zeolites," especially zeolite A and hydrated zeolite A materials, are useful for this purpose. A description of zeolite materials and a method of preparation appear in U.S. Pat. No. 2,882,243, Milton, issued April 14, 1959.

Also useful are aminophosphonate stabilizers, which are commercially available compounds sold under the names Dequest 2000, Dequest 2041 and Dequest 2060, by The Monsanto Company, St. Louis, Missouri.

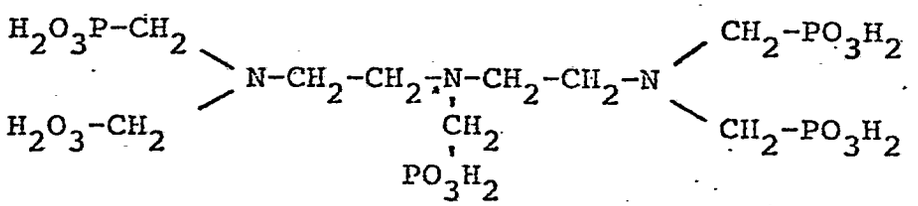
These compounds have the following structures:



Dequest 2000



Dequest 2041



Dequest 2060

In preferred compositions of the present invention the aminophosphonate compounds can be used in their acid form, represented by the above formulas, or one or more of the acidic hydrogens can be replaced by an alkali metal ion, e.g., sodium or potassium.

Additional stabilizers can also be used, primarily to protect the peroxyacids against decomposition which is catalyzed by heavy metals such as iron and copper. Such additional stabilizing agents are preferably present at levels of from 0.005% to 1.0% of the composition. These additional stabilizers can be any of the well-known chelating agents, but certain ones are preferred. U.S. Pat. No. 3,442,937, Sennewald et al., issued May 6, 1969, discloses a chelating system comprising quinoline or a salt thereof, an alkali metal polyphosphate, and optionally, a synergistic amount of urea. U.S. Pat. No. 2,838,459, Sprout, Jr., issued July 10, 1959, discloses a variety of polyphosphates as stabilizing agents for peroxide baths. These materials are useful herein. U.S. Pat. No. 3,192,255, Cann, issued June 29, 1965, discloses the use of quinaldic acid to stabilize percarboxylic acids. This material, as well as picolinic acid and dipicolinic acid, would also be useful in the compositions of the present invention. A preferred auxilliary chelating system for the present invention is a mixture of 8-hydroxyquinoline or dipicolinic acid and an acid polyphosphate, preferably acid sodium pyrophosphate. The latter may be a mixture of phosphoric acid and sodium pyrophosphate wherein the ratio of the former to the latter is from 0.2:1 to 2:1 and the ratio of the mixture of 8-hydroxyquinoline or dipicolinic acid is from 1:1 to 5:1. The foregoing patents relating to stabilizers are incorporated herein by reference.

Coatings

The dry granular compositions can be coated with coating materials in order to protect them against moisture and other environmental factors which may tend to cause deterioration of the compositions when stored for long periods of time. Such coating materials may be in general, acids, esters, ethers, surfactants and hydrocarbons and include such a wide variety of materials as fatty acids, derivatives of fatty alcohols such as esters and ethers, poly functional carboxylic acids and amides, alkyl benzene sulfonates, alkyl sulfates and hydrocarbon oils and waxes. These materials aid in preventing moisture from reaching the peroxyacid compound. Secondly, the coating may be used to segregate the peroxyacid compound from other agents which may be present in the composition and which could adversely affect the peroxyacid's stability. The amount of the coating material used is generally from 2.5% to 20% based on the weight of the peroxyacid compound.

Solubility Improvers

Agents which improve the solubility of the peroxyacid product such as sodium sulfate, starch, cellulose derivatives, surfactants, etc., are also advantageously used herein. (See U.S. Pat. No. 4,126,573, Johnson, issued November 21, 1978) These agents can be called solubilizers and are generally used in an amount of from 10% to 200% based on the weight of the peroxyacid.

Exotherm Control Agents

When subjected to excessive heat, organic peroxyacids can undergo a self-accelerating decomposition which can generate sufficient heat to ignite the peroxyacid. For this reason, it is desirable to include an exotherm control agent in peroxyacid bleaching compositions. Suitable

materials include urea, hydrates of potassium aluminum sulfate and aluminum sulfate. A preferred exotherm agent is boric acid (See U.S. Pat. No. 4,100,095, Hutchins, issued July 11, 1978). The exotherm agent is preferably used in the composition at a level of from 50% to 400% of the amount of peroxyacid.

Miscellaneous

Various other optional ingredients such as dyes, optical brighteners, perfumes, soil suspending agents and the like may also be used in the compositions herein at the levels conventionally present in detergent and bleaching compositions.

In the following examples, which are illustrative only and are not to be construed as limiting the invention, the Hunter Whiteness values set froth are a measure of the bleaching activity of the bleaching agents tested. The larger Hunter Whiteness value represents greater cleaning and whitening.

EXAMPLE 1

1. Preparation of the hydrophobic bleach composition. The hydrophobic peroxyacid, peroxylauric acid, was prepared by the oxidation of the parent carboxylic acid, lauric acid, with hydrogen peroxide in the presence of water and sulfuric acid. The CMC of sodium laurate equals 2×10^{-2} molar. Reaction conditions were typical of those cited in the literature (e.g., Parker et al., J. Am. Chem. Soc., 77, 4037 (1955). The resulting 70/30 peroxylauric acid-water mixture was blended with finely ground urea (3 parts urea to 1 part peroxylauric acid) and dried to form the peroxyacid adduct. The adduct was analyzed and determined to contain 1.7% AvO.

2. Preparation of the hydrotropic bleach composition. The hydrotropic peroxyacid, diperoxydodecanedioic acid, was prepared by the oxidation of dodecanedioic acid with hydrogen peroxide in the presence of sulfuric acid. Reaction conditions were typical of those cited in the literature (e.g., McCune Can. 635, 620). Neither the mono- or disodium salts of dodecanedioic acid has a measurable CMC below 0.5M and the parent acid has a retention time of 23.3 minutes under the chromatographic conditions previously cited. The diperoxyacid-water mixture resulting from the synthesis contained 34% peroxyacid. This mixture was blended with finely ground urea (3 parts urea to 1 part peroxyacid) and dried. The resulting chemical was partially adducted and was analyzed to contain 2.7% AvO.

3. Preparation of Bleaching Solution. A six liter, 100°F washing solution was used. Bleach product was weighed out according to the values in Table I to obtain the required AvO in the wash. Each bleach composition was added to the wash in combination with 1.5 g/l Tide detergent. The solution pH was adjusted to 8.5 with 10% solutions of either sodium hydroxide or sulfuric acid.

4. Preparation of Bleachable Stains. A representative hydrophilic stain was prepared when cotton swatches were stained with tea. Hunter Whiteness of the swatches was measured on a Hunter Color Meter. A representative hydrophobic stain was obtained by selecting normally soiled dingy T-shirts. 3" x 3" swatches were prepared from the bottom halves of the

T-shirts. Hunter Whiteness readings are recorded and the swatches were uniformly distributed between the three treatments shown in Table I.

5. Bleach Test. After execution of #3 for each of the three bleach compositions in Table I, 6 tea stains and/or 5-6 dingy T-shirt swatches were added and washed for 14 minutes. After rinsing, fabrics were dried and then final Hunter Whiteness values recorded. The average increase in Hunter Whiteness over all the fabrics is reported in Table I.

The results show that the mixture is superior to peroxylauric acid on hydrophilic stains and is superior to either individual component on hydrophobic stains. When the composite of results on both stains is considered, the mixture has an overall advantage over the individual components.

TABLE I

			Hunter Whiteness (avg.)	
Bleach	Gms/l	ppm AvO	Hydrophilic Tea Stains	Hydrophobic Dingy T-Shirts
PLA[1]	0.70	12	29	6.7
DPDA/PLA[2]	0.22 0.35	6 6	40	9.0
DPDA[3]	0.44	12	43	6.0

[1]Peroxylauric acid adduct;

[2]Diperoxydodecanedioic acid adduct; Peroxylauric acid adduct; and

[3]Diperoxydodecanedioic acid adduct.

EXAMPLE 2

1. Preparation of Hydrotropic Bleach Composition. The hydrotropic peroxyacid, diperoxytridecanedioic acid, was prepared by oxidation of tridecanedioic acid with hydrogen peroxide in the presence of sulfuric acid and water. Typical reaction conditions involve diluting 408g of concentrated sulfuric acid with water to 420g and with chilling, adding 80g of 50% hydrogen peroxide. 50g of tridecanedioic acid powder is added to the chilled solution with continuous agitation. Temperature of the reaction is raised slowly to 25-30°C and held for 2 hours. Reaction mix was chilled and quenched with 500g of cold H_2O. Crystals of diperoxydodecanedioic acid were collected and washed with water to remove sulfuric acid. The resulting product was a mixture of peroxyacid and water, which analyzed to contain 4.6% AvO. The mono- and disodium salts of tridecanedioic acid have no apparent CMC below 0.5M, and the parent acid has a retention time of 97 minutes under the previously cited chromatographic conditions.

2. Preparation of Hydrophilic Bleach Composition. The hydrophilic bleach, diperoxyadipic acid, was prepared by oxidation of adipic acid with hydrogen peroxide in the presence of sulfuric acid. Reaction conditions were typical of those cited in the literature (e.g., Parker et al., J. Am. Chem. Soc., 79, 1929 (1957). The mono- and disodium salts of adipic acid have no apparent CMC below 0.5M, and the parent acid has a retention time of 2.4 minutes under the previously cited chromatographic conditions. The diperoxyacid was further processed to make a granule. 25g of diperoxy adipic acid was mixed with 34g of boric acid, 140g

of anhydrous sodium sulfate and 21g of a surfactant paste. The paste contained approximately 28% C_{13} LAS, 22% sodium sulfate, and the remainder water. The paste contained typical peroxyacid stabilizers (0.1g dipicolinic acid, 0.05g sodium pyrophosphate and 0.05g phosphoric acid). After mixing the product was dried. Analysis showed that the granules contained 2.2% AvO.

3. Preparation of Bleach Solution and Bleachable Stains.

Bleach solution and bleachable stains were prepared the same as in Example 1. The bleach compositions used are listed in Table II. The results show an increase in bleaching efficacy on both the hydrophilic and hydrophobic stains for the mixture over the individual components. The mixture has an overall advantage over the individual components when both stains are considered.

TABLE II

			Hunter Whiteness (avg.)	
Bleach	Gms/l	ppm AvO	Hydrophilic Tea Stains	Hydrophobic Dingy T-Shirts
DPTA[1]	0.33	15	41	7.0
DPTA/ DPAA[2]	0.15 0.37	7 8	44.5	8.3
DPAA[3]	0.69	15	41	6.5

[1]Diperoxytridecanedioic acid

[2]Diperoxytridecanedioic acid/ Diperoxyadipic acid granule

[3]Diperoxyadipic acid granule

EXAMPLE 3

The preparation and properties of the hydrophilic bleach, diperoxyadipic acid, are described in Example 2, paragraph 2. The preparation and description of the hydrophobic peroxyacid, peroxylauric acid, are described in Example 1, paragraph 1. The preparation of the bleach solution and bleachable stains are as described in Example 1. The three bleach compositions are listed in Table III. The results show an increase in hydrophilic stain removal for the mixture over the individual components, and an increase in hydrophobic stain removal for the mixture over DPAA. When the composite of results on both stains is considered the mixture has an overall advantage over the individual components.

TABLE III

			Hunter Whiteness (avg.)	
Bleach	Gms/l	ppm AvO	Hydrophilic Tea Stains	Hydrophobic Dingy T-Shirts
PLA[1]	0.81	14	35	4.6
PLA/DPAA[2]	0.23 0.40	4 10	37.5	4.2
DPAA[3]	0.65	14	34.5	3.0

[1]Peroxylauric acid adduct;

[2]Peroxylauric acid adduct/ Diperoxyadipic acid granule; and

[3]Diperoxyadipic acid granule.

CLAIMS

1. A laundry bleach composition characterised in that it comprises a mixture of peroxyacid bleaches selected from:

a + b,
a + c,
b + c,
a + (b + c),
b + (a + c),
c + (a + b),

wherein "a" is a hydrophilic bleach which is most effective on hydrophilic soils,
wherein "b" is a hydrotropic bleach which is effective on both hydrophilic and hydrophobic soils, and wherein "c" is a hydrophobic bleach which is most effective on hydrophobic soils, and

wherein said peroxyacid bleaches in said mixture have a ratio of from 1:20 to 20:1 on a parts per million (ppm) available oxygen basis.

2. A composition according to Claim 1 wherein said ratio is from 10:1 to 1:10.

3. A composition according to either one of Claims 1 and 2 wherein said ratio is from 3:1 to 1:3.

4. A composition according to any one of Claims 1-3 wherein said mixture is perlauric acid and diperoxydodecanedioic acid.

5. A composition according to any one of Claims 1-3 wherein said mixture is perlauric acid and diperoxyadipic acid.

6. A composition according to any one of Claims 1-3 wherein said mixture is diperoxyadipic acid and diperoxytridecanedioic acid.

European Patent Office

EUROPEAN SEARCH REPORT

0068547
Application number

EP 82 20 0707.6

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
D,A	US - A - 4 126 573 (J. P. JOHNSTON)	
D,A	US - A - 4 100 095 (J.P. HUTCHINS et al.) & DE - A1 - 2 737 865	
A	US - A - 4 013 581 (A.E. HUBER) * claims 2, 3 *	
A	DE - A1 - 2 612 587 (PROCTER & GAMBLE CO.) * claims 1 to 4 *	

CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)

C 11 D 3/39
D 06 L 3/02

TECHNICAL FIELDS SEARCHED (Int.Cl. 3)

C 11 D 3/00
D 06 L 3/00

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
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A: technological background
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X The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Berlin	14-07-1982	SCHULTZE

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